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Formation of Conductive Networks with Both Segregated and Double-Percolated Characteristic in Conductive Polymer Composites with Balanced Properties

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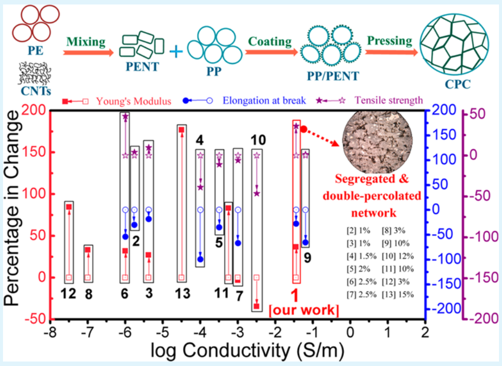
Supporting Information

ABSTRACT: Morphological control of conductive networks involves the construction of segregated or double-percolated conductive networks is often reported to reduce the electrical percolation threshold of conductive polymer composites (CPCs) for better balance among electrical conductivity, mechanical properties, and filler content. Herein, the construction of conductive networks with both segregated and double-percolated characteristics is achieved based on polypropylene (PP)/polyethylene (PE) and multi-wall carbon nanotubes (CNTs). CNTs were firstly dispersed in PE; then PE/CNTs were compounded with PP particles well below the melting temperature of PP. It is observed that the percolation threshold (p_c) decreases with increasing PP particle size (size 3.6 mm, p_c = 0.08 wt %), which agrees with previous theoretical prediction and experiment in much smaller particle size range. To further study this, the amount of CNTs in PE is varied. It is shown that the degree of PE/CNTs coating on PP particles varies with CNTs as well as PE content in these composites, and have significant influence on the final electrical property. Furthermore, a model combines classical percolation theory and model for segregated network has been proposed to analyze the effect of particle size, degree of coating and thickness of coating on the percolation behavior of these CPCs. In such a model the percolation of CNTs in PE phase as well as PENT phase in the segregated structure can be described. Overall, through such method, a much better balance among mechanical property, conductivity, and filler content is achieved in these CPCs comparing with the results in literature.



KEYWORDS: *conductive polymer composites, conductive network, segregated and double-percolated network, particle size, electrical percolation*

1. INTRODUCTION

Conductive polymer composites (CPCs) have generated intense interest due to their tunable properties, wide range of applications and ease of fabrication.[1−3] Conductive fillers (e.g. carbon nanotubes,[4] carbon black,[5] graphene,[6−8] etc.) are incorporated into various polymers to fabricate CPCs. With increasing conductive filler content, a jump in conductivity can be observed when a critical filler content is reached. This phenomenon is often termed electrical percolation, and the critical content is referred as percolation threshold (p_c). Relative high filler content can often lead to high conductivity in these CPCs. However, poor mechanical performance could be caused by filler aggregation at high content, not to mention their high cost and poor process-ability. To fabricate bulk CPCs with better balance among conductivity, mechanical properties, and filler content, strategies have been proposed to reduce p_c through morphological control of conductive networks formed with various conductive fillers.[6−13] Many methods have been demonstrated to be able to control these networks, resulting in different structural characteristics. For instance, using polymer blends can trigger the formation of networks with selective distribution in various phases;[14] using latex particle is able to trigger the formation of segregated networks;[15,16] methods involves strong shear often cause orientation in filler network;[17−19] thermal annealing above the melting temperature or glass transition temperature of polymer matrix can repair local conductive contacts.[20−22] Moreover, these methods can be combined to allow the construction of conductive networks with desired special structural features for various applications.[13,23−25] It has been widely demonstrated that these morphological control methods are crucial for their p_c and final electrical properties.[26]

Among these methods, double-percolated network through using polymer blends[27−29] and segregated network through using latex particles[16,30] have been shown to be prominently effective at allowing the formation of conductive networks with low filler content. In double-percolated networks, conductive fillers are selectively distributed in one of the polymer matrices

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or their interface in immiscible polymer blends.[13,25,27,29,31−34] In this structure, both the conductive filler network in the filler-rich phase and the continuity of such polymer phase are essential for maintaining the conductive network. In segregated networks, the conductive particles are located only at the interfaces between polymer particles, instead of being randomly distributed throughout the system.[30,35−41] Due to their tunable particle size and surface functionality, latex particle based composites that possess segregated network characteristic have been intensively investigated in the past decade to achieve ultra-low percolation threshold.[15,16,30,40,42] Such low percolation threshold can be achieved thanks to the fact that conductive fillers are constrained at the interface between these polymer domains in such a segregated structure, leading to the formation of conductive networks at relative low filler content. Therefore, the polymer domain size of such structure is thought as very important issue as the amount of interface in the system increases with decreasing domain size. Larger interface area indicates more interface needs to be occupied by conductive filler to form network, thus, higher percolation threshold. Nevertheless, few studies paid attention to the influence of polymer particle size in segregated system on the percolation behavior and final electrical property.[16] Moreover, the particle sizes in these systems are often in the range of nanometers, which gives plenty of room to improve in terms of reducing the amount of interface through using larger polymer domain. Furthermore, one of the drawbacks for latex particle based CPCs is their poor mechanical performance caused by poor interfacial adhesion between different particles.[30,31,43] To enhance the mechanical properties of CPCs with segregated conductive networks, it is illustrated that the use of polymer in the interface could enhance the interfacial interaction between different domains.[10] This indicates that the use of polymer blends in these CPCs containing segregated network is beneficial for the electrical as well as mechanical properties. However, CPCs with both segregated and double-percolated networks are barely studied, and general guidelines for the design and preparation of these CPCs with balanced properties containing conductive networks in such configuration is still needed. Finally, the percolation behavior of bulk CPCs can be described by models such as classical percolation theory, and the percolation in segregated networks has been described by a theory proposed by Malliaris and Turner.[44] There is need to modify above models in order to describe the percolation behavior of conductive networks with both segregated and double-percolated characteristics.

Herein, attempts will be made to construct segregated and double-percolated networks in polymer blends based on polypropylene (PP)/polyethylene (PE) with CNTs as conductive filler. Firstly, CNTs will be selectively distributed in PE phase, and consequent compounded with PP well below the melting temperature of PP to keep the original PP particle size and prevent migration of CNTs from PE to PP phase. The size of PP particle is varied to study the effect of particle size on the percolation behavior in these CPCs. Additionally, the amount of CNTs in PE is varied to study the degree of PE/CNTs coating on PP particles. Furthermore, a model that combines the classical percolation theory and model for segregated network from Turner et al.[44] is proposed to study the percolation behavior of these CPCs.

2. EXPERIMENTAL SECTION

2.1. Materials. Multi-walled carbon nanotubes (CNTs, Nanocyl 7000) were obtained from Nanocyl S.A. (Belgium). These CNTs have a diameter of 10 nm, length of 1.5 mm, and a surface area of 250–300 m^2/g according to the producer. Three different sizes of PP were used as polymer matrix in this study, and the diameter is referred to as particle size throughout this study. The isotactic polypropylene (LPP, T30S) with an average particle size of ~3600 μm (the largest among all in this study) has a M_w of 3.9×10^5 g/mol and melt flow index (MFI) of 1.0 g/10 min. It was supplied by Dushanzi Co. Ltd., China, and used as received. The middle sized polypropylene (MPP) with an average particle size of ~2470 μm was prepared by processing and pelletizing LPP in two-screw extruder. Polypropylene powder (SPP), with the smallest particle size of ~898 μm, has melt flow index (MFI) of 1.0 g/10 min. It was supplied by Ningxia Baota Co. Ltd., China, and used as received. The high density polyethylene (HDPE, 2911, with $M_w = 1.3 \times 10^5$ g/mol, MFI = 20 g/10 min) was provided by Fushun Petro-chemical Corp. Maleic anhydride grafted polyethylene (trademarked as C-19, Westlake Chemical, U.S.A.) was used in PENT composites as compatibilizer to enhance the dispersion of CNTs. C-19 has an acid number of 5 mg KOH/g and molecular weight of 15 000 according to the producer.

2.2. Sample Preparation. Firstly, composites with 3, 5, 7 wt % of CNTs and 10 wt % C-19 was obtained by blending CNTs and HDPE in an internal mixer (XSS-300, Qingfeng Mold Factory, Shanghai, China) at 200 °C, at 60 rpm for 5 min. Then, these PENT composites containing 3, 5, and 7 wt % of CNTs with a format of black erose solid were then blended with PP particles in different sizes at desired weight contents (1−30 wt %) in the internal mixer at 145 °C, 50 rpm for 5 min. Such temperature is between the melting temperature of PE and PP. It was chosen in order to melt PENT phase and keep the original shape of PP during compounding, giving rise to the wrapping of PP particles with PENT melt. The composites were then hot-pressed (KT-0701, Kangte Technology Co. Ltd, Beijing, China) into samples at 200 °C at 10 MPa for 5 min. The experimental procedure is summarized in Figure 1A. For comparison, neat PP particles were processed under the same condition to minimize the impact of processing history on the properties.

In this paper, samples were denoted as *x*PP/PENT*y*-*z*, where *x* represents PP particle type, *y* represents CNTs content in PE, *z* represents the weight content of PENT in the composites. For example, LPP/PENT5-9% represents the polymer matrix is LPP, 9 wt % PENT is contained in this blend and the corresponding CNTs content in PE phase is 5 wt %.

2.3. Characterization. To study the morphology of these CPCs, scanning electron microscopy (SEM) study was carried out on cryo-fractured surfaces, which was sputter coated with gold and observed under a field emission SEM (Inspect F, FEI, Finland), with an accelerating voltage of 20 kV. A Leica DMIP optical microscope (OM) was used to inspect the degree of PENT coating on LPP particles. These photos were processed using software to calculate the coating degree of each particle. Five particles of each sample were inspected and processed to give an average value. The morphology of segregated network of PP/PENT composites was also investigated with a Leica DMIP optical microscope (OM), with the press-molded bars cut into films with a thickness of 100 μm, using a microtome (Leica RM2245).

The specimens for mechanical property measurement were prepared by hot-compaction at 200 °C, 10 MPa for 5 min, and standard tensile tests were performed using an SANS Universal tensile test machine with a crosshead speed of 50.00 mm/min. Five specimens of each group of sample were tested to give an average value.

Rheological measurement was performed on a Gemini 200 dynamic rheometer (Malvern Instruments Ltd., U.K.). Disk samples with a thickness of 1.2 mm and diameter of 25 mm were prepared by compression molding at 200 °C for 3 min. The rheological experiments were conducted at 200 °C over the frequency range 0.1−100 rad s^{-1} and at a shear strain of 1 %, within the linear viscoelastic region.

Contact angles were measured in a sessile drop mold with KRUSS DSA100. Specimens for contact angle measurements were compression molded at 200 ºC under 10 MPa for 10 min. Contact angles were measured on 3 mL of wetting solvent at 23 °C, and the results reported were the mean values of 3 replicates. The surface tensions,

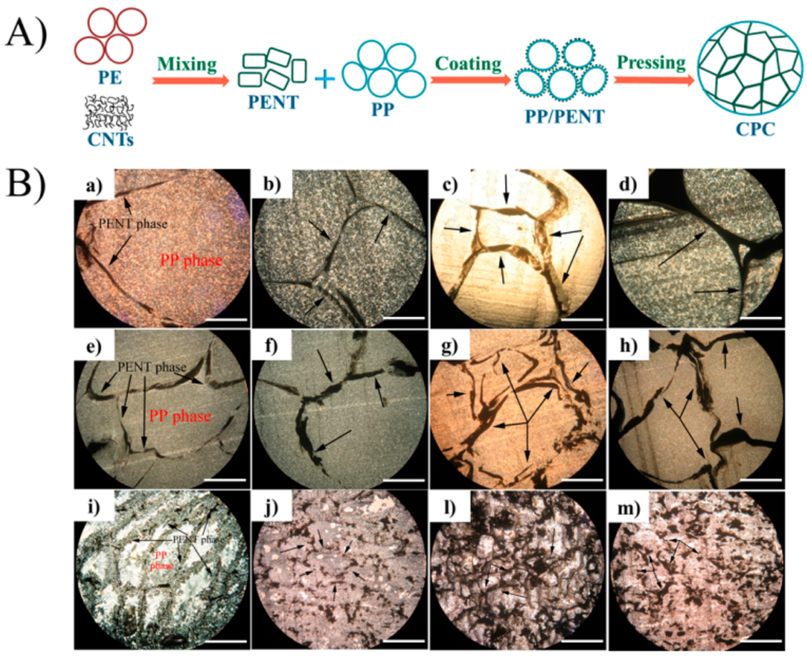

Figure 1. (A) Schematic description of the processing procedure for preparation of PP/PENT composites; (B) OM images of PP/PENT5 composites as a function of polymer particle sizes and PENT5 contents: a) LPP/PENT5-2%; b) LPP/PENT5-5%; c) LPP/PENT5-9%; d) LPP/PENT5-15%; e) MPP/PENT5-2%; f) MPP/PENT5-5%; g) MPP/PENT5-9%; h) MPP/PENT5-15%; i) SPP/PENT5-2%; j) SPP/PENT5-5%; k) SPP/PENT5-9%; l) SPP/PENT5-15%. The scale bar in above images stands for 1 mm. The arrows in those images point to the PENT phase in the composite.

dispersion, and polar components of these samples can be also obtained from contact angle measurements.

Direct current (DC) electrical resistivity was measured for the composites at room temperature. The two points method was used. Silver paint was applied onto both ends of the sample to ensure good contact. As a result, contact resistance was negligible compared with the resistance of the specimen. The electrical resistance was measured with a Keithley 6487 picoammeter at a constant voltage of 1 V. The results were recorded after the voltage had been exerted for 5 s. Resistivity can be calculated using the resistance by the following formula: $\rho = Rwt/l$, where R is the resistance of the sample, w, t, and l represent width, thickness, and length of the sample, respectively. Dimensions of the samples were $50 \times 40 \times 10$ mm^3 (lwt). Resistivity exceeding 10^4 Ω·m is not measurable with the current set-up and these specimens were therefore classified as nonconductive. Thereof, the reciprocal of resistivity yields conductivity.

3. RESULTS AND DISCUSSION

3.1. Influence of the Polymer Particle Size. *3.1.1. Morphology of the Network.* To observe the morphology of these CPCs, OM study is performed. Figure 1B shows optical micrographs of PP/PENT5 composites. These images clearly demonstrate that typical segregated and double-percolated structure has been constructed, where PENT-based conductive channels surrounding PP particles in different particle sizes throughout the composites are observed. The thickness of PENT conductive channels is noted to increase with its content once the polymer particle size is fixed. Figure 1B,a–d displays that PENT composites are located only between the matrix boundaries in LPP/PENT5 composites. In LPP/PENT5 and MPP/PENT5 composites, although the magnification in these images was limited to show the whole morphology of the specimens (see Figure 1B,a–h), bridged conductive pathways can be observed. In Figure 1B,i–m, the overall morphology of segregated and double-percolated network are more pronounced for SPP with the smallest particle size.[10,11,45]

As shown in Figure 1B,a,e,i, it is apparent that the amount of conductive pathways augments with polymer particle size decreasing from ~3600 μm to ~898 μm for the same PENT concentration. Meanwhile, the thickness of PENT channels surrounding PP particles sequentially decreases and the boundaries between polymer particles are more visually obvious. This indicates that segregated and double-percolated network can be constructed in these CPCs with their morphology effectively tuned through using polymer particles in different sizes.

Wu et al.[46] reported a plasma-etch technique for preparing SEM samples could give rise to better contrast between fillers and matrix, leading to a distinct morphological characterization. In this work, it is apparent that the microstructure of these conductive networks can already be inspected using conventional method shown in Figure 2. It should be interesting to use such technique in the future to obtain more detailed information on the network. Taking 9 wt % PENT5 coated PP as an example, Figure 2 displays the local morphology of these segregated and double-percolated conductive networks. It is noted that the boundaries between PP particles are clear, which indicates the migration of CNTs from PENT to PP phase during processing is prohibited. Besides, CNTs are rather evenly dispersed in PE phase. This is likely caused by the maleic anhydride grafted polyethylene added in the composites. Furthermore, the interfacial adhesion between PP granules was significantly enhanced by the presence of conductive PENT binder, resulting in segregated and double-percolated conductive networks with good mechanical performance (shown in Supporting Information Figure S1).

3.1.2. Electrical Properties of the Composites. Figure 3a–c demonstrates the conductivity as a function of overall CNTs weight fraction in PP/PE composites for CPCs with three different polymer particle sizes. The insects in each figure shows

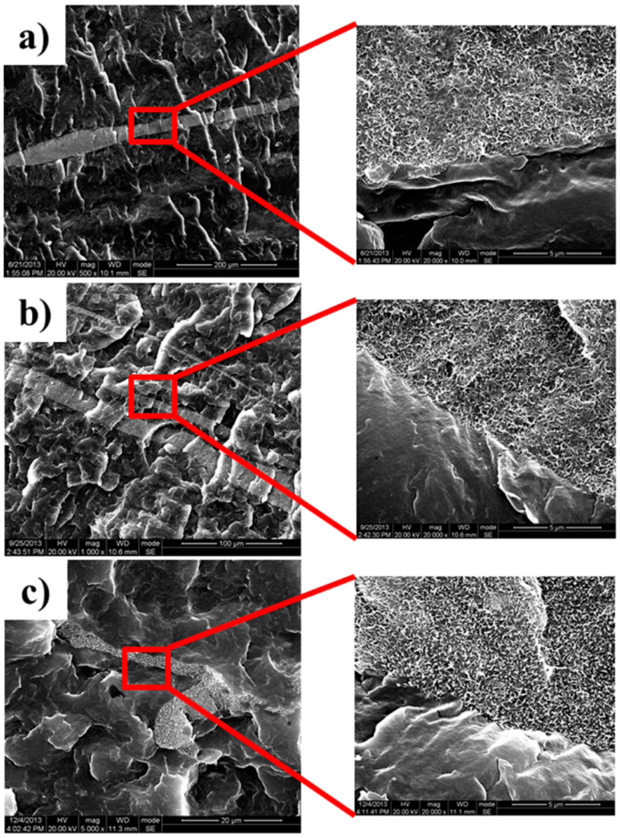

Figure 2. SEM micrographs of the segregated and double-percolated network in PP/PENT5-9% composites with the polymer matrix of (a) LPP; (b) MPP; (c) SPP.

the fitting lines and data according to classical percolation theory:[47]

$$\sigma = \sigma_0(p - p_c)^t, \quad p > p_c \tag{1}$$

where σ_0 is a scaling factor, p_c is the percolation threshold, σ is the conductivity and p is the filler content in CPCs. The exponent t is a parameter which depends on the dimensionality of conductive network. It is expected to vary for different materials with calculated values of $t \approx 1-1.3$ and $t \approx 1.6-2$ for two-and three-dimensional networks, respectively. As widely reported in literature,[9,20] p_c of CPCs can be determined accurately, and t can be obtained through fitting of classical percolation theory to experimentally obtained conductivity data. Using the data in Figure 3a−c, t is estimated to be 1.94 for LPP/PENT5, 1.90 for MPP/PENT5, and 1.50 for SPP/PENT5 system, which implies the presence of an approximate three-dimensional conductive network. Furthermore, the percolation threshold is observed to be 0.08, 0.14, and 0.33 wt % for segregated and double-percolated LPP/PENT5, MPP/PENT5, and SPP/PENT5 composites, respectively. As expected, such segregated and double-percolated structure generates a percolation threshold as low as 0.08 wt % for PP/PE composite. This is much lower than that of double-percolated PP/PE blends in our previous work (1.2 wt %).[13] Moreover, it is important to note that larger amount of CNTs is required to reach p_c and the same conductivity for CPCs containing smaller polymer particle size. This behavior can be explained by the greater amount of surface area associated with smaller polymer particles, which creates a random, less segregated microstructure.[16]

In theory, polymer particle size can be used to tailor percolation threshold. For a compacted mixture of polymer and conductive particles, the percolation threshold is expected to decrease with increasing ratio of polymer to conductive particle size according to Malliaris and Turner:[44]

$$p_c = 50A\left[1 + B\left(\frac{R_p}{R_m}\right)\right]^{-1} \tag{2}$$

where p_c is the critical content of conductive filler necessary to impart macroscopic composite electrical conductivity (i.e., the

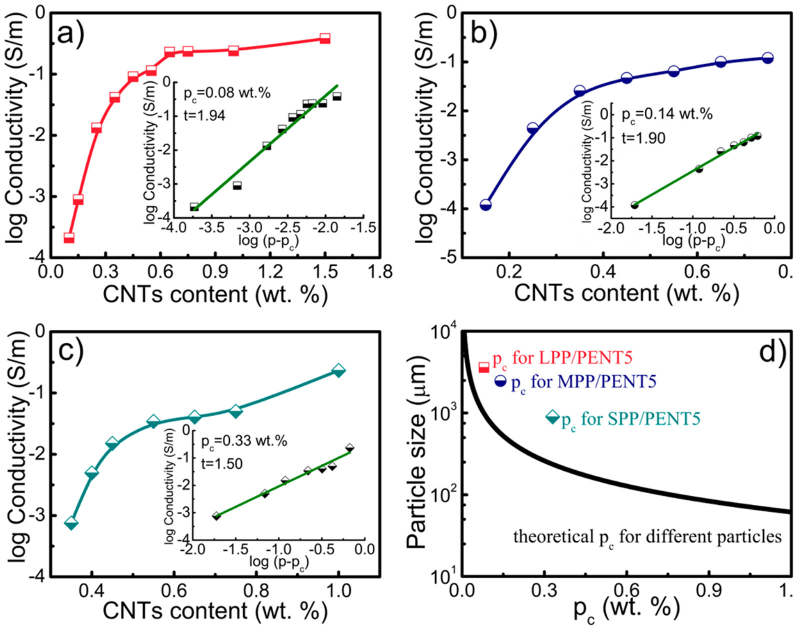

Figure 3. Electrical conductivities of PP/PENT5 composites with different PP particles: (a) LPP; (b) MPP; (c) SPP. Insets are the fitting lines according to the classical percolation theory. (d) Respective percolation thresholds as a function of polymer particle size; the line represents the predicted threshold using eq 2 and 1.32 μm for PENT coating thickness (It is determined by putting the experimental value of p_c and R_p of LPP system into eq 2 to calculate the value of R_m).

percolation threshold), A and B are constants related to the distribution and packing of conductive filler, R_p is the radius of polymer particle, and R_m is the radius of conductive particle (in this work, it represents the PENT coating thickness). In this case, the constants A and B are 0.33 and 0.2775, which correspond to hexagonal packing of PENT conductive coatings to produce the smallest threshold values.[16]

Figure 3d shows the decreasing trend of percolation threshold with increasing polymer particle size. LPP/PENT5 composites has almost a quarter the threshold (0.08 wt %) of SPP/PENT5 composites (0.33 wt %). The solid line represents the prediction of percolation threshold using eq 2. In this case, it is assumed that the PENT coating thickness in those three systems is the same (1.32 μm) here, and the variation of this parameter will be discussed in following study. A theoretical polymer particle size of 960 μm, which is much smaller than the experimental polymer particle size, is needed to obtain the same percolation threshold for LPP/PENT5 composites. It is shown that the theoretical conductive particle size is smaller than the experimental ones and this discrepancy can be explained by the construction of conductive particles formed by PE-based CNTs composites instead of pure CNTs (as assumed by the model[44]). Therefore, with the same R_m of conductive particles, the conductivity of PENT composites must be much lower than the pure CNT bundles and experimentally more CNTs are required to reach p_c.

In order to better understand the relationship between polymer particle size and electrical conductivity of these CPCs, the electrical percolation of CNTs in PE phase and the electrical percolation of PENT phase in the overall composites are considered together. Therefore, eqs 1 and 2 are combined to give rise to a new equation:

$$\sigma = \sigma_0\left(p - 50A\left[1 + B\left(\frac{R_p}{R_m}\right)\right]^{-1}\right)^t \tag{3}$$

In eq 3, both the percolation of CNTs in PE phase as well as percolation through formation of segregated network can be described. Similar method considering classic percolation and dynamic percolation has been proposed by Alig and his coworkers.[48,49] Through this equation, the electrical conductivity of one composite can be predicted once the polymer particle size and conductive filler size are determined. The feasibility of this method is examined using the data of this work. Figure 4 displays the experimentally obtained electrical conductivities and predicted conductivities of MPP/PENT5 and SPP/PENT5 composites. It is clearly shown that the deviation between the experimental and theoretical data is insignificant. Therefore, it is reasonable to use eq 3 as an auxiliary tool to predict the conductivity in advance.

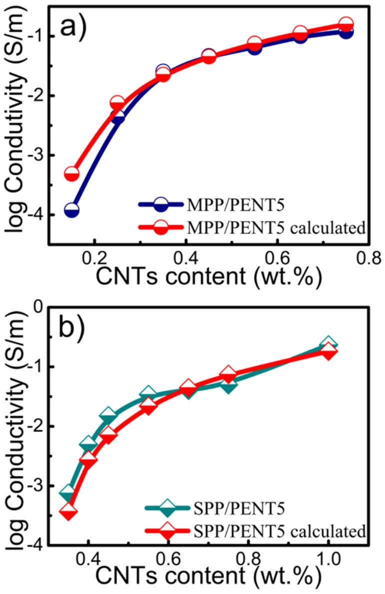

Figure 4. Experimental and predicted conductivities of (a) MPP/PENT5 composites and (b) SPP/PENT5 composites.

3.2. Influence of the PENT Coating Degree. In the above discussion, it was assumed that the thickness of PENT conductive coating and degree of coating (a parameter can be used to describe how well the PP domains are coated with PENT) are constant for different filler content. However, these two parameters are variable due to change in the viscosity of polymer matrices and compatibility between matrix and conductive phase, leading to different electrical percolation behavior. Therefore, exploring the effect of coating degree is necessary.

As well known, the viscosity of PE/CNT composites can be altered through adding CNTs;[23] therefore, the CNT content in PE phase is varied with the hope to change the degree of PENT coating on PP domains. Herein, CNT contents in PE range from 3, 5, to 7 wt %, and the viscosities of these composites are shown in Figure 5. With additional CNTs in PE, the rheological behavior is altered with higher viscosity than that of neat PE and PP. Besides, the viscosity of PENT composites obviously increases with increasing CNT content, and this phenomenon could be the premise of different PENT coating condition on PP particles. Figure 6 shows the conductivity of LPP/PENT composites with segregated and double-percolated network as a function of overall CNT content. It is interesting to note that LPP/PENT composites with the same overall CNT content shows different electrical properties. At the same overall CNT content, the conductivity of LPP/PENT3 composite is higher than that of LPP/PENT7 composite, and LPP/PENT5 is the lowest among them. In these double-percolated and segregated conductive networks, the conductivity of LPP/PENT composites is influenced by the following two issues: PENT coating degree and perfection of the segregated and double-percolated network. The coating conditions of LPP/PENT composites with various PENT contents are revealed in Supporting Information (Figure S2) using OM observation and the corresponding SEM

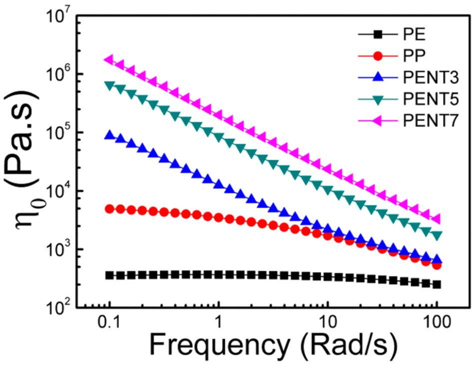

Figure 5. Dynamic viscosity of neat PE, PP, and PENT with different CNTs content as a function of frequency.

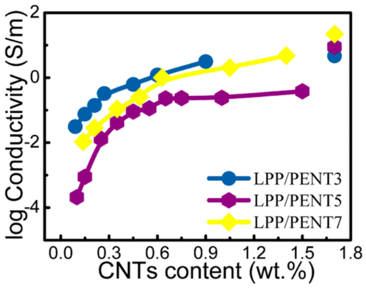

Figure 6. Conductivity of LPP/PENT composites with different CNTs contents in PE phase. The data marker on the right side of this figure shows the conductivity of PE/CNTs composite formed with homogenerous conductive network, with the CNTs content is 3 wt % (circle), 5 wt % (hexagon), and 7 wt % (square).

Table 1. PENT Coating Degrees of LPP Particles with the PENT Contents are 2, 5, 9, and 15 wt %

	2%	5%	9%	15%
LPP/PENT3	42.30	59.06	76.49	89.02
LPP/PENT5	39.45	44.42	66.49	84.52
LPP/PENT7	39.09	43.18	58.92	77.20

images are shown in Supporting Information (Figure S3). By processing images in Figure S2, the PENT coating degree can be obtained and the corresponding data is listed in Table 1. It is demonstrated that the data of coating degree augments with the increment of PENT content in the system where CNT content in PE phase is fixed. The coating degree decreases gradually with increasing CNT content once PENT content is unaltered. This is in accordance with the observation in Supporting Information Figures S2 and S3. It is speculated that the PENT coating degree is dominated by two factors: CNT content in PE and PENT content. Besides, the degree of coating increases with increasing PENT content while the increment of CNT content in PE causes inferior flow-ability for PENT to coat on LPP particle, giving rise to poor coating condition. Therefore, the degree of coating influenced by the above two factors can be expressed by the following equation:

$$f(p, p_{\mathrm{m}}) = C\frac{p^{m}}{p_{\mathrm{m}}^{n}} \tag{4}$$

where p represents the overall CNT content in the composite and p_{m} represents CNT content in PE phase. C is a constant, and m and n are parameters.

Besides, it is worth noticing that even with the lowest CNT content in PE, coating degree can not reach 100%. The reason for this is that the surface energy difference between PP and PE is not low enough for PENT to wet PP domains completely. The interfacial energies (see Table 2) can be evaluated from the surface tensions of the components, using both harmonic-mean and geometric-mean equations.[50] The harmonic-mean equation (eq 5) is valid between low-energy materials and the geometric-mean equation (eq 6) is valid between a low-energy material and a high-energy material:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4\left(\frac{\gamma_1^{\mathrm{d}}\gamma_2^{\mathrm{d}}}{\gamma_1^{\mathrm{d}} + \gamma_2^{\mathrm{d}}} + \frac{\gamma_1^{\mathrm{p}}\gamma_2^{\mathrm{p}}}{\gamma_1^{\mathrm{p}} + \gamma_2^{\mathrm{p}}}\right) \tag{5}$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\sqrt{\gamma_1^{\mathrm{d}}\gamma_2^{\mathrm{d}}} + \sqrt{\gamma_1^{\mathrm{p}}\gamma_2^{\mathrm{p}}}\right) \tag{6}$$

Table 2. Surface Tension and Interfacial Energy Results of LPP and PENT Specimens with Various CNT Contents

	surface tensions (mN/m)			interfacial energies with LPP (mN/m)	
				calculation methods	
materials	total (γ)	dispersive part (γ^{d})	polar part (γ^{p})	harmonic	geometric
LPP	49.9	38.9	11.0		
PENT3	47.2	33.6	13.6	0.66	0.33
PENT5	37.4	32.1	5.3	2.68	1.37
PENT7	35.0	30.0	5.0	3.42	1.76

where γ_1, γ_2 are the surface tensions of components 1, 2; γ_1^{d}, γ_2^{d} are the dispersive parts of the surface tensions of components 1, 2; and γ_1^{p}, γ_2^{p} are the polar parts of surface tensions of components 1, 2. For these two methods, the calculated wetting coefficients are positive (and even above 1, see Table 2), as the interfacial energy between LPP and PENT3 is slightly lower than those between LPP and PENT5, and between LPP and PENT7, which indicates a slightly better wetting of PENT with LPP. It is noted that there is a dramatic change in interfacial energy between LPP/PENT3 and LPP/PENT5, and an explanation is needed. Given that the CNT contents in PENT5 is higher than in PENT3, more and more CNT bundles could appear on the PE surface, leading to a coarser surface, which greatly increases the interfacial energy between PENT and LPP. Therefore, the PENT3 tends to coat LPP more easily than the other two PENTs.

As well known, the conductivity of CPCs is proportional to the number of conductive pathways,[51−53] and the probability of network formation is proportional to conductivity.[54] Given that $f(p,p_{\mathrm{m}})$ is the effective conductive area concentration, where the conductive network exists, the conductivity is regarded as directly related with the effective conductive area (degree of coating). Therefore, the classical percolation scaling law can be modified as follows in order to better describe the percolation behavior of these CPCs:

$$\sigma = \sigma_0(p - p_{\mathrm{c}})^t f(p, p_{\mathrm{m}}) \tag{7}$$

Another parameter—thickness of PENT coating on LPP particle—is also affected by the coating degree and PENT content in the composite. Increasing PENT content can increase conductive layer thickness, yet with a certain PENT content, increasing coating degree leads to decreasing conductive layer thickness. Thus, the thickness of conductive layer can be expressed by following equation:

$$R_{\mathrm{m}} = D\frac{p/p_{\mathrm{m}}}{f(p, p_{\mathrm{m}})} \tag{8}$$

where D is a constant. Therefore, with the consideration of conductive layer coating condition, relationship between the conductivity of composites formed by segregated and double-percolated conductive network and polymer matrix particle size can be expressed with eq 9, which is the combination of eqs 3, 4, 7, and 8:

$$\sigma = \sigma_0\left(p - 50A\left[1 + B\left(\frac{R_{\mathrm{p}}}{D\frac{p\,/\,p_{\mathrm{m}}}{C(p^{\mathrm{m}}\,/\,p_{\mathrm{m}}^{\mathrm{n}})}}\right)\right]^{-1}\right)^{t} C(p^{m}/p_{\mathrm{m}}^{n}) \tag{9}$$

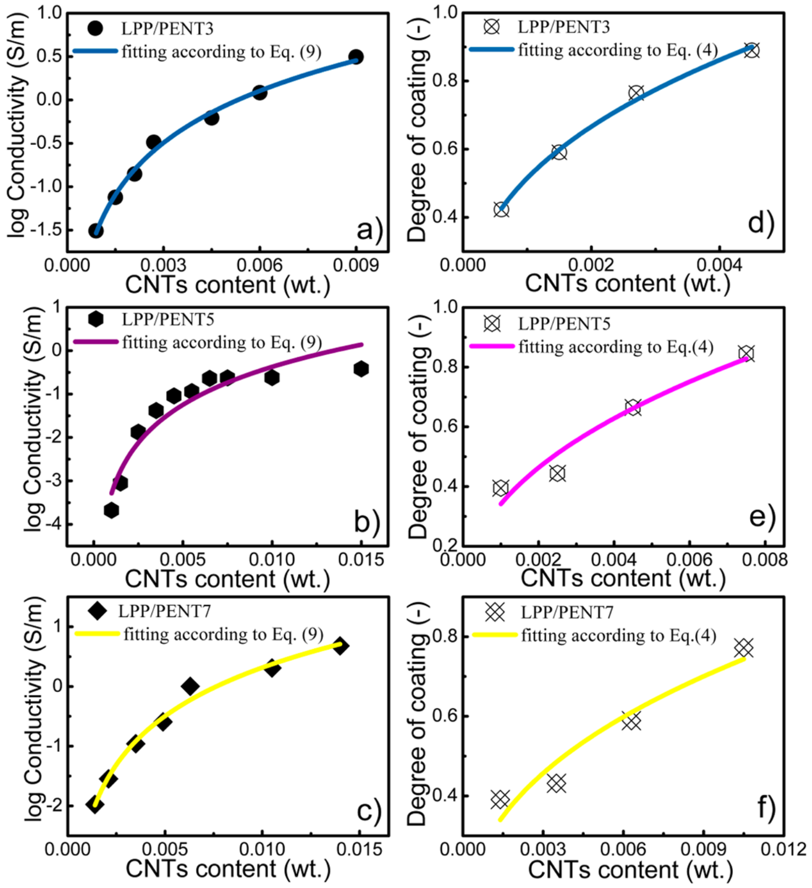

Figure 7. Fitting curves of conductivity for (a) LPP/PENT3; (b) LPP/PENT5; and (c) LPP/PENT7 composites according to eq 9. (d, e, f) Fitting curves of the coating degree of corresponding composites according to eq 4.

As shown in Figure 7, the percolation behavior of LPP/PENT3, LPP/PENT5, and LPP/PENT7 composites can be described using above equations. The fitted parameters for these percolation curves are listed in Table 3. It is obvious to note that the values of C (which represents the constant of PENT coating degree) decrease with increasing CNT contents in PE phase. This agrees well with the results of OM observation in Supporting Information Figure S3 and coating degree data in Table 1.

Table 3. Fitted Parameters of the LPP/PENT Composites According to the Modified Classical Percolation Theory

	C	*D*	*m*	*n*
LPP/PENT3	1.59	1.72	0.37	0.41
LPP/PENT5	0.53	2.21	0.44	0.87
LPP/PENT7	0.39	2.50	0.39	0.99

In addition, the thickness of conductive layer in each specimen can be obtained through calculating the attained values of parameters using eq 8, and the curves of theoretical R_m are plotted in Figure 8a. It clearly displays that R_m increases with increasing PENT content within the same system; R_m of LPP/PENT7 composites seem to be the highest amongst three systems with LPP/PENT5 composites well below. LPP/PENT3 composites have the lowest R_m. As discussed above, with a certain PENT content, the decrement of coating degree leads to increasing R_m; it is shown in Table 1 that the coating degree of LPP/PENT7 is much lower than that of LPP/PENT5 once the PENT content is above 9 wt %, thus, it is expected that the R_m of LPP/PENT7 composites is much higher than that of LPP/PENT5 composites. However, the calculated thickness of conductive layer in LPP/PENT7

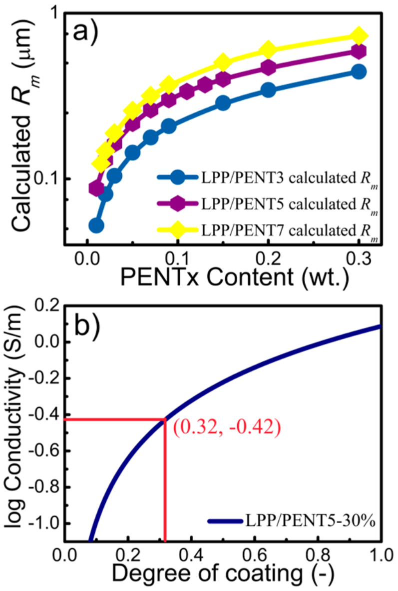

Figure 8. (a) Calculated R_m in three systems as a function of PENT content; (b) predicted conductivity of LPP/PENT5-30% composite as a function of PENT coating degree, and the coordinate indicates the predicated coating degree of the LPP/PENT5-30% specimen with experimentally obtained conductivity.

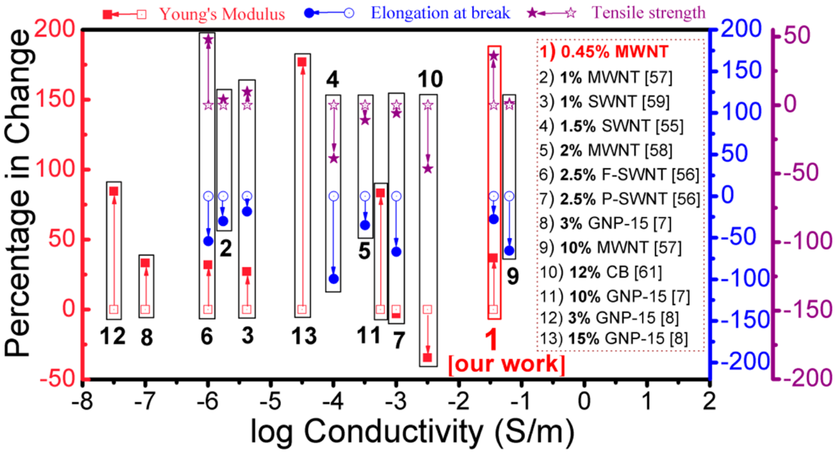

Figure 9. Percentage in change of mechanical property as a function of electrical conductivity, compared with other papers.[7,8,55−59,61] The polymer matrices are PP for refs 7, 55−59; PE for ref 8; and poly(vinyl acetate) for ref 61.

composites is only slightly enhanced comparing to LPP/PENT5. The mechanism responsible for this phenomenon is that the viscosity of PE with 7 wt % CNTs is higher than those of PE filled with 3 or 5 wt % CNTs[23] and the interfacial energy between PENT7 and LPP is the highest as indicated in Table 2. This agrees well with experimental observation shown in Supporting Information Figure S4, where the coating of PENT phase on PP domains is not uniform for PE containing 7 wt % CNTs and the presence of non-effective PENT agglomerates is observed throughout the conductive network, which barely contributes to the electrical property of these composites. The situation for PE containing 3 and 5 wt % of CNTs is similar to each other, where effective conductive networks are formed. Furthermore, as shown in Figure 8b, the conductivity of LPP/PENT5-30% composite with different coating degree is predicted through eq 9 using the fitted parameter of LPP/PENT5 in Table 3. It is indicated that the conductivity increases with increasing PENT coating degree; a 100 % coating degree yields a conductivity of 1.22 S/m, which is more than 10 times higher than one with only 10 % coating degree, thus coating degree of PENT plays an important role in determining the final electrical property. Another function of this prediction is that the coating degree of conductive layer can be predicted with known overall conductivity. In Figure 8b, a coating degree of 32 % for LPP/PENT5-30% composite is predicted with a log conductivity of −0.42.

Finally, to understand the overall performance for these CPCs, the mechanical properties, conductivity and filler content of our CPCs is plotted to compare with some results reported in literature (as shown in Figure 9). It can be noted that with only 0.45 wt % MWNT filled in PP, an increase in Young's modulus of 36.8 % and an enhancement in tensile strength of 35.9 % are obtained in current study, which is much larger than the results reported previously.[55−59] Although the tensile strength improvement is larger than that of this work, the composite with 2.5 wt % F-MWNT is non-conductive,[56] while the conductivity of PP/0.45 wt % MWNTs in this study can reach 0.036 S/m. Comparing with the composites with slightly higher conductivity, the concentration of MWNTs is almost 22 times as much as used in current research, and the ductility is seriously damaged.[57] Polyolefin/GNP composites seem to have superior flexural moduli no matter the filler content is low (3 vol %) or high (10 or 15 vol %),[7,8] yet the electrical conductivities of the composites is lower than that in our system. Besides, poor mechanical performance is caused by porosity and poor interfacial adhesion in latex based systems.[30,60,61] The physical property of poly(vinyl acetate) composite prepared by latex technology is shown to be seriously damaged by the addition of carbon black.[61] Overall, PP composites with better balance between electrical property, filler content and mechanical property can be fabricated through such a method combining segregated and double-percolated network structure. It can be used as a general guideline for the preparation of high performance CPCs with balanced properties. Future development to enhance the degree of coating by various methods and the improvement in process-ability (injection molding processable) could lead to industrial application in the near future.

4. CONCLUSIONS

In this work, CPCs with segregated and double-percolated networks containing PE/CNTs as conductive component in PP matrix is fabricated. The prepared composites exhibit percolation values as low as 0.08 wt % and better balance between conductivity, mechanical properties and filler content is achieved comparing with other bulk CPCs reported in literature. The influences of polymer matrix particle size and the coating degree of the conductive layer on the electrical conductivity of the composites are thoroughly investigated. Polymer matrix with larger particle size is shown to have lower percolation threshold, and coating degree plays an important role on the percolation behavior. A model combines classical percolation theory and theory for segregated network is proposed to describe the percolation behavior in these CPCs. It is demonstrated that this model agrees well with experimental results and can be used as a tool to analyze the percolation behavior of these CPCs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Five figures of mechanical property, optical micrographs of coating condition, scanning electron micrographs of coating condition, optical observation of network, and DSC curves of the composites. The material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Alig, I.; Potschke, P.; Lellinger, D.; Skipa, T.; Pegel, S.; Kasaliwal, G. R.; Villmow, T. Establishment, Morphology, and Properties of Carbon Nanotube Networks in Polymer Melts. *Polymer* **2012**, *53*, 4−28.

(2) Bauhofer, W.; Kovacs, J. Z. A Review and Analysis of Electrical Percolation in Carbon Nanotube Polymer Composites. *Compos. Sci. Technol.* **2009**, *69*, 1486−1498.

(3) Pham, V. H.; Dang, T. T.; Hur, S. H.; Kim, E. J.; Chung, J. S. Highly Conductive Poly (Methyl Methacrylate)(PMMA)-Reduced Graphene Oxide Composite Prepared by Self-Assembly of PMMA Latex and Graphene Oxide through Electrostatic Interaction. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2630−2636.

(4) Dalmas, F.; Dendievel, R.; Chazeau, L.; Cavaille, J. Y.; Gauthier, C. Carbon Nanotube-Filled Polymer of Electrical Conductivity in Composites: Numerical Simulation Three-Dimensional Entangled Fibrous Networks. *Acta Mater.* **2006**, *54*, 2923−2931.

(5) Cao, Q.; Song, Y.; Tan, Y.; Zheng, Q. Conductive and Viscoelastic Behaviors of Carbon Black Filled Polystyrene During Annealing. *Carbon* **2010**, *48*, 4268−4275.

(6) Wu, H.; Rook, B.; Drzal, L. T. Dispersion Optimization of Exfoliated Graphene Nanoplatelet in Polyetherimide Nanocomposites: Extrusion, Precoating, and Solid State Ball Milling. *Polym. Compos.* **2013**, *34*, 426−432.

(7) Kalaitzidou, K.; Fukushima, H.; Drzal, L. T. A New Compounding Method for Exfoliated Graphite−Polypropylene Nanocomposites with Enhanced Flexural Properties and Lower Percolation Threshold. *Compos. Sci. Technol.* **2007**, *67*, 2045−2051.

(8) Jiang, X.; Drzal, L. T. Reduction in Percolation Threshold of Injection Molded High-Density Polyethylene/Exfoliated Graphene Nanoplatelets Composites by Solid State Ball Milling and Solid State Shear Pulverization. *J. Appl. Polym. Sci.* **2012**, *124*, 525−535.

(9) Zhang, S.; Lin, L.; Deng, H.; Gao, X.; Bilotti, E.; Peijs, T.; Zhang, Q.; Fu, Q. Synergistic Effect in Conductive Networks Constructed with Carbon Nanofillers in Different Dimensions. *Express Polym. Lett.* **2012**, *6*, 159−168.

(10) Pang, H.; Bao, Y.; Ding, X. Y.; Chen, C.; Wang, J. H.; Li, Z. M. Double-Segregated Carbon Nanotube/Polymer Conductive Composites as Candidates for Liquid Sensing Materials. *J. Mater. Chem. A* **2013**, *1*, 4177−4181.

(11) Pang, H.; Yan, D. X.; Bao, Y.; Chen, J. B.; Chen, C.; Li, Z. M. Super-Tough Conducting Carbon Nanotube/Ultrahigh-Molecular-Weight Polyethylene Composites with Segregated and Double-Percolated Structure. *J. Mater. Chem.* **2012**, *22*, 23568−23575.

(12) Ma, P. C.; Liu, M. Y.; Zhang, H.; Wang, S. Q.; Wang, R.; Wang, K.; Wong, Y. K.; Tang, B. Z.; Hong, S. H.; Paik, K. W. Enhanced Electrical Conductivity of Nanocomposites Containing Hybrid Fillers of Carbon Nanotubes and Carbon Black. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1090−1096.

(13) Gao, X.; Zhang, S.; Mai, F.; Lin, L.; Deng, Y.; Deng, H.; Fu, Q. Preparation of High Performance Conductive Polymer Fibres from Double Percolated Structure. *J. Mater. Chem.* **2011**, *21*, 6401−6408.

(14) Ji, M.; Deng, H.; Yan, D.; Li, X.; Duan, L.; Fu, Q. Selective Localization of Multi-Walled Carbon Nanotubes in Thermoplastic Elastomer Blends: An Effective Method for Tunable Resistivity-Strain Sensing Behavior. *Compos. Sci. Technol.* **2014**, *92*, 16−26.

(15) Yoonessi, M.; Gaier, J. R. Highly Conductive Multifunctional Graphene Polycarbonate Nanocomposites. *ACS Nano* **2010**, *4*, 7211−7220.

(16) Moriarty, G. P.; Whittemore, J. H.; Sun, K. A.; Rawlins, J. W.; Grunlan, J. C. Influence of Polymer Particle Size on The Percolation Threshold of Electrically Conductive Latex-Based Composites. *J. Polym. Sci., Polym. Phys.* **2011**, *49*, 1547−1554.

(17) Li, N.; Cheng, W.; Ren, K.; Luo, F.; Wang, K.; Fu, Q. Oscillatory Shear-Accelerated Exfoliation of Graphite in Polypropylene Melt During Injection Molding. *Chin. J. Polym. Sci.* **2013**, *31*, 98−109.

(18) Gao, Y.; Zong, G.; Bai, H. Combined Effects of Stretching and Nanofillers on The Crystalline Structure and Mechanical Properties of Polypropylene and Single-Walled Carbon Nanotube Composite Fibers. *Chin. J. Polym. Sci.* **2014**, *32*, 245−254.

(19) Bin, Y.; Mine, M.; Koganemaru, A.; Jiang, X.; Matsuo, M. Morphology and Mechanical and Electrical Properties of Oriented PVA−VGCF and PVA−MWNT Composites. *Polymer* **2006**, *47*, 1308−1317.

(20) Deng, H.; Bilotti, E.; Zhang, R.; Loos, J.; Peijs, T. Effect of Thermal Annealing on The Electrical Conductivity of High-Strength Bicomponent Polymer Tapes Containing Carbon Nanofillers. *Synthetic Met.* **2010**, *160*, 337−344.

(21) Deng, H.; Skipa, T.; Bilotti, E.; Zhang, R.; Lellinger, D.; Mezzo, L.; Fu, Q.; Alig, I.; Peijs, T. Preparation of High-Performance Conductive Polymer Fibers through Morphological Control of Networks Formed by Nanofillers. *Adv. Funct. Mater.* **2010**, *20*, 1424−1432.

(22) Zhang, S.; Lin, L.; Deng, H.; Gao, X.; Bilotti, E.; Peijs, T.; Zhang, Q.; Fu, Q. Dynamic Percolation in Highly Oriented Conductive Networks Formed With Different Carbon Nanofillers. *Colloid Polym. Sci.* **2012**, *290*, 1393−1401.

(23) Yu, F.; Deng, H.; Zhang, Q.; Wang, K.; Zhang, C.; Chen, F.; Fu, Q. Anisotropic Multilayer Conductive Networks in Carbon Nanotubes Filled Polyethylene/Polypropylene Blends Obtained Through High Speed Thin Wall Injection Molding. *Polymer* **2013**, *54*, 6425−6436.

(24) Wen, M.; Sun, X.; Su, L.; Shen, J.; Li, J.; Guo, S. The Electrical Conductivity of Carbon Nanotube/Carbon Black/Polypropylene Composites Prepared Through Multistage Stretching Extrusion. *Polymer* **2012**, *53*, 1602−1610.

(25) Li, B.; Zhang, Y. C.; Li, Z. M.; Li, S. N.; Zhang, X. N. Easy Fabrication and Resistivity-Temperature Behavior of an Anisotropically Conductive Carbon Nanotube−Polymer Composite. *J. Phys. Chem. B* **2009**, *114*, 689−696.

(26) Deng, H.; Lin, L.; Ji, M.; Zhang, S.; Yang, M.; Fu, Q. Progress on the Morphological Control of Conductive Network in Conductive Polymer Composites and the Use as Electroactive Multifunctional Materials. *Prog. Polym. Sci.* **2013**, DOI: org/10.1016/j.progpolymsci.2013.07.007.

(27) Gubbels, F.; Jérôme, R.; Vanlathem, E.; Deltour, R.; Blacher, S.; Brouers, F. Kinetic and Thermodynamic Control of the Selective Localization of Carbon Black at the Interface of Immiscible Polymer Blends. *Chem. Mater.* **1998**, *10*, 1227−1235.

(28) Goldel, A.; Marmur, A.; Kasaliwal, G. R.; Potschke, P.; Heinrich, G. Shape-Dependent Localization of Carbon Nanotubes and Carbon Black in an Immiscible Polymer Blend During Melt Mixing. *Macromolecules* **2011**, *44*, 6094−6102.

(29) Thongruang, W.; Spontak, R. J.; Balik, C. M. Bridged Double Percolation in Conductive Polymer Composites: An Electrical Conductivity, Morphology, and Mechanical Property Study. *Polymer* **2002**, *43*, 3717−3725.

(30) Grunlan, J. C.; Gerberich, W. W.; Francis, L. F. Electrical and Mechanical Behavior of Carbon Black-Filled Poly (Vinyl Acetate) Latex-Based Composites. *Polym. Eng. Sci.* **2001**, *41*, 1947−1962.

(31) Li, Y.; Shimizu, H. Conductive PVDF/PA6/CNTs Nanocomposites Fabricated By Dual Formation of Cocontinuous and Nanodispersion Structures. *Macromolecules* **2008**, *41*, 5339−5344.

(32) Sumita, M.; Sakata, K.; Asai, S.; Miyasaka, K.; Nakagawa, H. Dispersion of Fillers and the Electrical Conductivity of Polymer Blends Filled with Carbon Black. *Polym. Bull.* **1991**, *25* (2), 265−271.

(33) Feller, J. Conductive Polymer Composites: Influence of Extrusion Conditions on Positive Temperature Coefficient Effect of Poly(butylene terephthalate)/Poly(olefin)−Carbon Black Blends. *J. Appl. Polym. Sci.* **2004**, *91*, 2151−2157.

(34) Wu, G.; Miura, T.; Asai, S.; Sumita, M. Carbon Black-Loading Induced Phase Fluctuations in PVDF/PMMA Miscible Blends: Dynamic Percolation Measurements. *Polymer* **2001**, *42*, 3271−3279.

(35) Mu, M.; Walker, A. M.; Torkelson, J. M.; Winey, K. I. Cellular Structures of Carbon Nanotubes in a Polymer Matrix Improve Properties Relative to Composites With Dispersed Nanotubes. *Polymer* **2008**, *49*, 1332−1337.

(36) Zhang, C.; Ma, C. A.; Wang, P.; Sumita, M. Temperature Dependence of Electrical Resistivity for Carbon Black Filled Ultra-High Molecular Weight Polyethylene Composites Prepared by Hot Compaction. *Carbon* **2005**, *43*, 2544−2553.

(37) Hu, H.; Zhang, G.; Xiao, L.; Wang, H.; Zhang, Q.; Zhao, Z. Preparation and Electrical Conductivity of Graphene/Ultrahigh Molecular Weight Polyethylene Composites with a Segregated Structure. *Carbon* **2012**, *50*, 4596−4599.

(38) Jurewicz, I.; Worajittiphon, P.; King, A. A.; Sellin, P. J.; Keddie, J. L.; Dalton, A. B. Locking Carbon Nanotubes in Confined Lattice Geometries−A Route to Low Percolation in Conducting Composites. *J. Phys. Chem. B* **2011**, *115*, 6395−6400.

(39) Moriarty, G. P.; Wheeler, J. N.; Yu, C.; Grunlan, J. C. Increasing the Thermoelectric Power Factor of Polymer Composites Using a Semiconducting Stabilizer for Carbon Nanotubes. *Carbon* **2012**, *50*, 885−895.

(40) Grunlan, J. C.; Mehrabi, A. R.; Bannon, M. V.; Bahr, J. L. Water-Based Single-Walled-Nanotube-Filled Polymer Composite with an Exceptionally Low Percolation Threshold. *Adv. Mater.* **2004**, *16*, 150−153.

(41) Grunlan, J. C.; Gerberich, W. W.; Francis, L. F. Electrical and Mechanical Behavior of Carbon Black-Filled Poly(Vinyl Acetate) Latex-Based Composites. *Polym. Eng. Sci.* **2001**, *41*, 1947−1962.

(42) Yu, C.; Kim, Y. S.; Kim, D.; Grunlan, J. C. Thermoelectric Behavior of Segregated-Network Polymer Nanocomposites. *Nano Lett.* **2008**, *8*, 4428−4432.

(43) Wu, M.; Shaw, L. L. On the Improved Properties of Injection-Molded, Carbon Nanotube-Filled PET/PVDF Blends. *J. Power Sources* **2004**, *136*, 37−44.

(44) Malliaris, A.; Turner, D. Influence of Particle Size on the Electrical Resistivity of Compacted Mixtures of Polymeric and Metallic Powders. *J. Appl. Phys.* **1971**, *42*, 614−618.

(45) Pang, H.; Chen, C.; Bao, Y.; Chen, J.; Ji, X.; Lei, J.; Li, Z. M. Electrically Conductive Carbon Nanotube/Ultrahigh Molecular Weight Polyethylene Composites With Segregated and Double Percolated Structure. *Mater. Lett.* **2012**, *79*, 96−99.

(46) Wu, H.; Drzal, L. T. Graphene Nanoplatelet−Polyetherimide Composites: Revealed Morphology and Relation to Properties. *J. Appl. Polym. Sci.* **2013**, *130*, 4081−4089.

(47) Stauffer, D.; Aharony, A. *Introduction to Percolation Theory*; Taylor and Francis: London, 1985.

(48) Alig, I.; Skipa, T.; Engel, M.; Lellinger, D.; Pegel, S.; Potschke, P. Electrical Conductivity Recovery in Carbon Nanotube Polymer Composites after Transient Shear. *Phys. Status Solidi B* **2007**, *244*, 4223−4226.

(49) Alig, I.; Lellinger, D.; Engel, M.; Skipa, T.; Pötschke, P. Destruction and Formation of a Conductive Carbon Nanotube Network in Polymer Melts: In-Line Experiments. *Polymer* **2008**, *49*, 1902−1909.

(50) Fenouillot, F.; Cassagnau, P.; Majeste, J. C. Uneven Distribution of Nanoparticles in Immiscible Fluids: Morphology Development in Polymer Blends. *Polymer* **2009**, *50*, 1333−1350.

(51) Lin, L.; Zhang, Q.; Liu, S.; Li, X.; Ji, M.; Deng, H.; Fu, Q. Towards Tunable Sensitivity of Electrical Property to Strain for Conductive Polymer Composites Based on Thermoplastic Elastomer. *ACS Appl. Mater. Interfaces* **2013**, *5*, 5815−5824.

(52) Simmons, J. G. Generalized Formula for the Electric Tunnel Effect between Similar Electrodes Separated by a Thin Insulating Film. *J. Appl. Phys.* **1963**, *34*, 1793.

(53) Zhang, X. W.; Pan, Y.; Zheng, Q.; Yi, X. S. Time Dependence of Piezoresistance for the Conductor-Filled Polymer Composites. *J. Polym. Sci. Polym. Phys.* **2000**, *38*, 2739−2749.

(54) Kyrylyuk, A. V.; van der Schoot, P. Continuum Percolation of Carbon Nanotubes in Polymeric and Colloidal Media. *P. Natl. A. Sci.* **2008**, *105*, 8221−8226.

(55) Moore, E. M.; Ortiz, D. L.; Marla, V. T.; Shambaugh, R. L.; Grady, B. P. Enhancing The Strength of Polypropylene Fibers With Carbon Nanotubes. *J. Appl. Polym. Sci.* **2004**, *93*, 2926−2933.

(56) McIntosh, D.; Khabashesku, V. N.; Barrera, E. V. Nanocomposite Fiber Systems Processed From Fluorinated Single-Walled Carbon Nanotubes and a Polypropylene Matrix. *Chem. Mater.* **2006**, *18*, 4561−4569.

(57) Zhou, Z.; Wang, S.; Zhang, Y.; Zhang, Y. Effect of Different Carbon Fillers on The Properties of PP Composites: Comparison of Carbon Black with Multiwalled Carbon Nanotubes. *J. Appl. Polym. Sci.* **2006**, *102*, 4823−4830.

(58) Xiao, Y.; Zhang, X.; Cao, W.; Wang, K.; Tan, H.; Zhang, Q.; Du, R.; Fu, Q. Dispersion and Mechanical Properties of Polypropylene/Multiwall Carbon Nanotubes Composites Obtained via Dynamic Packing Injection Molding. *J. Appl. Polym. Sci.* **2007**, *104*, 1880−1886.

(59) Manchado, M.; Valentini, L.; Biagiotti, J.; Kenny, J. Thermal and Mechanical Properties of Single-Walled Carbon Nanotubes-Polypropylene Composites Prepared by Melt Processing. *Carbon* **2005**, *43*, 1499−1505.

(60) Miltner, H. E.; Grossiord, N.; Lu, K.; Loos, J.; Koning, C. E.; Van Mele, B. Isotactic Polypropylene/Carbon Nanotube Composites Prepared by Latex Technology: Thermal Analysis of Carbon Nanotube-Induced Nucleation. *Macromolecules* **2008**, *41*, 5753−5762.

(61) Grunlan, J.; Bloom, F.; Gerberich, W.; Francis, L. Effect of Dispersing Aid on Electrical and Mechanical Behavior of Carbon Black-Filled Latex. *J. Mater. Sci. Lett.* **2001**, *20*, 1523−1526.