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Electric field-induced alignment of MWCNTs during the processing of PP/MWCNT composites: effects on electrical, dielectric, and rheological properties

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Abstract: High-frequency electric field (HEF) was applied to prepare aligned carbon nanotube (CNT)-reinforced polypropylene (PP) matrix composites during the compression molding process in this article. The effects of the alignment of multiwalled CNTs (MWCNTs) in the PP matrix under HEF on the electrical, dielectric, and rheological properties of the resulting composites were reported. The results showed that the composites prepared in the presence of the electric field had better conductivity than those of the untreated composites. The dielectric property measurement indicates that MWCNTs aligning along the direction of the imposed electric field greatly improved the dielectric properties of composites. Rheological analysis showed that the storage modulus of the aligning direction samples is higher than the value of the untreated composites and the microstructure of the composite has been changed due to the effect of HEF.

Keywords: alignment; high-frequency electric field; microstructure; multiwalled carbon nanotubes; properties.

1 Introduction

Due to their exceptional electrical, mechanical, thermal, and magnetic properties coupled with high aspect ratio and large interfacial contact area, carbon nanotubes (CNTs) have been treated as ideal candidates for achieving or enhancing the functional properties of polymer-based composites by compounding with various polymeric matrices [1]. With the addition of CNTs and other conductive fillers, the conductive polymer-based composite materials possess both the conductivity of the filler and the favorable processability of the polymer material.

It is known that the internal structure determines the properties of conductive composites. The electrical and mechanical properties of polymer-based composites, which are filled with 1D CNTs, are strongly dependent on their structure, particularly on their orientation degree. Conductive composites incorporated with oriented particle may exhibit excellent property in filler orientation, which can be potentially applied for the field of unidirectional product. However, the conductive CNTs will be dispersed and arranged randomly in polymer matrix without the external action, and the prepared composites are unable to take full advantage of the excellent performance of CNTs, which severely constrain the applications of CNTs/polymer composites in many fields. Hence, incorporating the aligning CNTs to take advantage of their exceptional anisotropic properties is an effective means to further promote the properties of CNT/polymer composites.

A lot of techniques, including mechanical force [2–4], magnetic field [5, 6], shear flows [7, 8], electrospinning [9, 10], and electric field [11–16], have been used to align CNTs. Electric field has been demonstrated as an efficient approach to manipulate CNTs. A pair of facing parallel plate electrodes, in which the CNT/polymer composites are sandwiched, is typically used for the application of the electric field [17]. The mechanism that manipulates the alignment of CNTs under the electric field consists of two basic effects: electrophoresis and dielectrophoresis. In the applied electric field, in virtue of the electrophoresis of CNTs, the dipole moments are induced in the nanotubes, causing the CNTs to rotate, orient, and move toward the nearest electrode. As a result, the charged CNTs are able to migrate and the CNT network is stretched across the electrodes to provide a conductivity pathway throughout the sample to facilitate the alignment of CNTs within the polymer [12]. The other is the dielectrophoresis of CNT, which is produced by the polarization of individual conductive nanotubes induced by an electric field. This polarization has contributed components in the parallel and radial directions of the CNT axis, whereas the polarizability of the parallel direction is greater than that in the radial direction [13]. This differential polarizability enables CNTs to have a certain torque under the

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electric field and is also the reason for CNTs to overcome the viscous resistance provided by polymer-based melts during the aligning process.

The previously reported works on electric field-induced CNTs alignment are primarily in polymer solution or during the curing process of thermosetting resins. Gupta et al. [13] tried to align CNTs in polyvinylidene difluoride (PVDF) solution by applying external alternating voltage and alternating pulsed current during the fabrication process. They concluded that the voltage-assisted alignment led to the alignment of CNTs inside the PVDF matrix, whereas the current assisted the alignment of CNTs by joining them to be end-to-end. However, there have been only a few reports referring to that electric field-induced alignment and conductive pathway formation of CNTs in polymer-based melts. Zhang et al. [11] used the dynamic percolation measurement to investigate the formation and dissociation of multiwalled CNT (MWCNT) conductive pathways induced by an electric field in the PC melt. There can be observed a sharp reduction in resistivity on exposure to 500 V/cm, whereas electrical resistivity increases rapidly as electric field ramps down to 1 V/cm. The explanation of this phenomenon is that the torque acting on MWCNTs is insufficient against the force coming from Brownian motion, which makes MWCNTs return to the random state again.

In this work, the alignment of polypropylene (PP)/MWCNT composites is achieved by high-frequency electric field (HEF). A self-developed HEF processing device is employed in this research to manipulate the alignment and conductive pathway formation of MWCNTs in the PP matrix under the molten state. MWCNTs are assumed to form linear paths along the direction of the electric field between the electrodes for the direct passage of current. We intended to investigate the effect of HEF on MWCNT alignment and the microstructure of the filler-matrix in composites. Also, the effect of MWCNT alignment on the electrical, dielectric, and rheological properties of

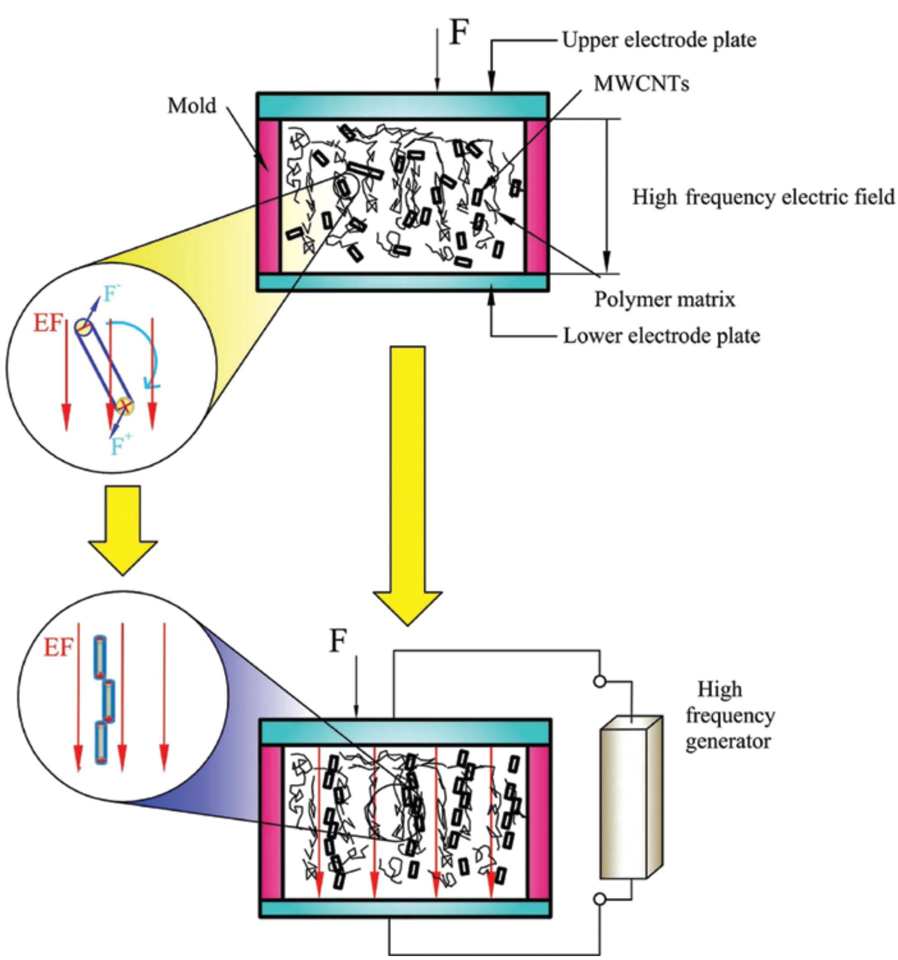

Figure 1: Schematic drawing of the HEF processing device.

PP/MWCNT composites are reported via various characterization methods.

2 Materials and methods

2.1 Materials

PP (T30S) with a melt flow index of 3.0 g/10 min was supplied by Sinopec Group (China). MWCNTs (XFM16) were purchased from Nanjing XFNANO Materials Tech Co., Ltd. (China). These MWCNTs presented an inner diameter of 5–10 nm, an outer diameter of 10–20 nm, a length of 0.5–2 μm, and a specific surface area of about 200 m^2/g.

2.2 Sample preparation

The materials (PP and MWCNTs) were dried at 80°C for 4 h in an oven before use. PP/MWCNT composite materials were prepared by mixing PP pellets with MWCNT powder using a Brabender mixer at 180°C for 20 min. The MWCNT weight fractions were 0.1%, 0.5%, 1%, 2%, 3%, 4% and 5%. The mixtures were moved in a self-developed HEF processing device for hot-compression molding. The device is schematically shown in Figure 1. The inducing HEF was established between two plates connected to a high-frequency generator (GJ5-6B-I-JY). The high-frequency generator could provide an output voltage up to 7 kV. The mixtures were made into 1-mm-thick plates of PP/MWCNT composites by hot-compression molding at 180°C with a pressure of 12 MPa for 12 min. HEF was applied in the last 4 min during the hot-pressing process when the composites were in molten stage. After processing, composite plates were quenched immediately in cold water to prevent MWCNTs from returning to the random state again.

2.3 Characterization

2.3.1 Morphology observation

Transmission electron microscopy (TEM) observations were carried out using a JEM-1400 Plus at an acceleration voltage of 120 kV. Ultrafine sample cuts were prepared with a thickness of 70 nm using a Leica EMUC6/FC6 microtome. A scanning electron microscopy (SEM; Quanta 250, FEI, USA) was used to observe the fractured surface morphology of samples. Samples were prepared from the molded specimens by fracturing in liquid nitrogen and coating with gold before examination.

2.3.2 AC electrical conductivity and dielectric property measurement

AC electrical conductivity and dielectric properties were measured with an Agilent 4294A impedance analyzer

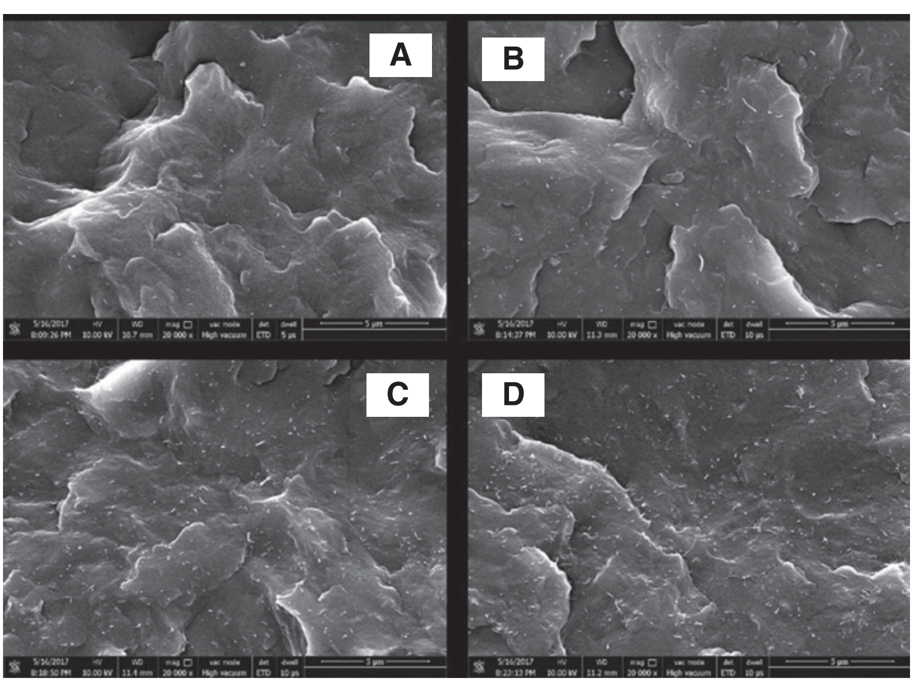

Figure 2: SEM images of untreated PP/MWCNT composites: (A) 0.5% MWCNTs, (B) 1% MWCNTs, (C) 2% MWCNTs and (D) 3% MWCNTs.

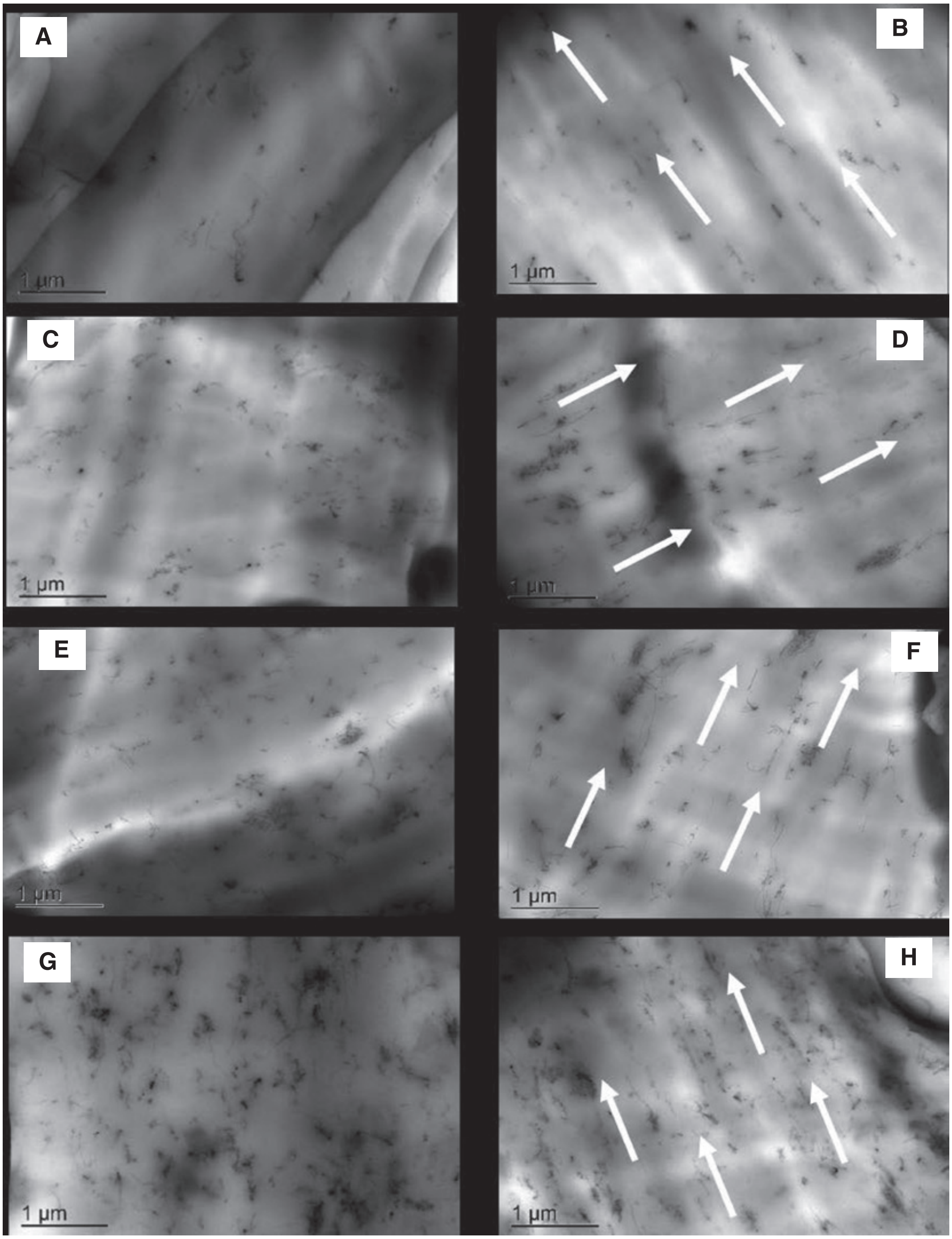

Figure 3: TEM images of PP/MWCNT composites with and without the applied HEF: (A) 0.5% MWCNTs, (B) 0.5% MWCNTs + HEF, (C) 1% MWCNTs, (D) 1% MWCNTs + HEF, (E) 2% MWCNTs, (F) 2% MWCNTs + HEF, (G) 3% MWCNTs and (H) 3% MWCNTs + HEF.

at ambient temperature within the frequency range of 1–100 kHz and 1 kHz–1 MHz, respectively. The specimens were coated with low-temperature silver paste for good contact between the specimen and the electrode. Three specimens were tested for each sample and the average values were reported.

2.3.3 Rheological property analysis

Disk-shaped specimens with a thickness of 1 mm and a diameter of 25 mm were prepared and the rheological behavior of the PP/MWCNT samples was measured on Physica MCR302 rheometer from Anton Paar equipped with a CTD620 convection oven. The samples were tested at 200°C with a scanning frequency range of 0.01–628 rad/s.

3 Results and discussion

3.1 Morphology of PP/MWCNTs

Figure 2 shows the SEM images of PP/MWCNT composites with MWCNT content of 0.5, 1, 2, and 3 wt.%. The dispersion of MWCNTs is relatively homogeneous in the PP matrix and few aggregates of MWCNTs can be observed. Figure 3 shows the TEM images of the ultrathin section of PP/MWCNT composites with MWCNT concentration of 0.5, 1, 2 and 3 wt.% prepared with and without HEF. In the TEM images, MWCNTs are distributed uniformly in the PP matrix. However, the orientation of MWCNTs is irregular in the composites without treatment by HEF (Figure 3A, C, E and G), whereas they show a distinct alignment in the composites with applied HEF, as marked by white arrows in Figure 3B, D, F and H. For samples with 0.5 wt.% MWCNTs, because the content is low, the aligning MWCNTs are almost isolated from one another and have no obvious contacts to generate the conductive pathways. Once the concentration of MWCNTs reaches 1 and 2 wt.%, there can be seen the presence of agglomerates (Figure 3B–F). After the application of the electric field, however, MWCNTs align distinctly and overlap with each other (Figure 3D and F). When MWCNTs increase to 3 wt.%, more aggregations of MWCNTs can be observed in two types of composite, which obviously form a conductive network in the matrix.

3.2 Electrical conductivity

Figure 4A shows the frequency dependence of AC electrical conductivity measured within the frequency range of 10^3–10^5 Hz for untreated PP/MWCNT composites with MWCNT content of 0.1–5 wt.% at room temperature. The AC electrical conductivity of all composites with 0.1–2 wt.% MWCNTs increase linearly with increasing frequency in the AC electrical conductivity-frequency plotting, indicating typical insulator behavior and the capacitance-dominant mechanism [18]. For the composites with MWCNT content of more than 2 wt.%, its AC electrical conductivity curve appears to be a plateau and remains nearly constant with increasing frequency, which means the formation of a 3D interconnecting network by dispersed MWCNTs within PP matrices. If the MWCNT content is higher than the percolation value, the conductivity is mainly determined by the numerous paths formed by the percolating clusters rather than the capacitors. Therefore, the conductivity of these composites will not change with increasing frequency, and a plateau appears in AC conductivity-frequency plots [19].

Figure 4B shows the frequency dependence of AC electrical conductivity measured within the frequency range of 10^3–10^5 Hz for HEF-treated PP/MWCNT composites with MWCNT content of 0.1–5 wt.% at room temperature. The AC electrical conductivity of all composites with 0.1–1 wt.% MWCNTs increase linearly with increasing frequency. However, when the MWCNT content is 2 wt.%, its curve is different with the untreated sample, and the AC electrical conductivity remains constant with increasing frequency, which means the formation of conductive networks is brought forward to 2 wt.% when the composite samples are processed under the effect of HEF.

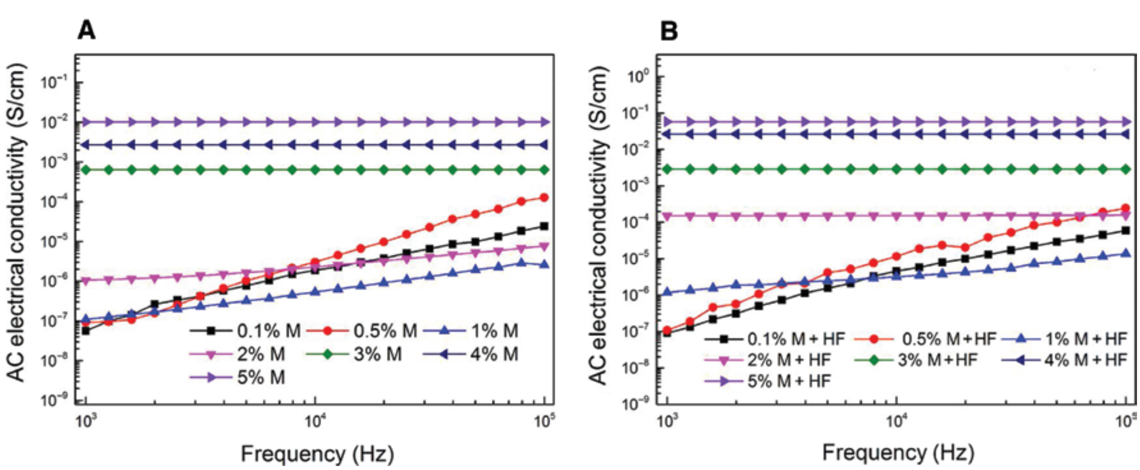

Figure 4: Frequency dependence of AC electrical conductivity of PP/MWCNT composites with different MWCNT contents at room temperature: (A) untreated and (B) HEF treated.

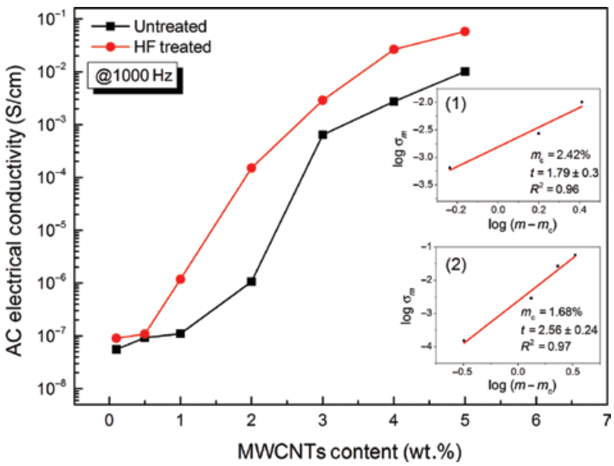

Figure 5: AC conductivity versus MWCNT content of PP/MWCNT composites with and without the applied HEF at 1000 Hz.
The insets show the plot of log σ_m vs. log $(m-m_c)$ [(1) untreated and (2) HF treated] and the straight line represents the best-fitted line of the data in Eq. (1).

The AC conductivity result at 10^3 Hz of PP/MWCNT composites with and without the applied HEF is plotted in Figure 5 as a function of the MWCNT concentration. One can divide both plots into three regions. With increasing MWCNT content up to 0.5 wt.%, the exertion of HEF has little lifting effect on σ. This is because when the MWCNT content is relatively low, it is too far to form a conductive network, although MWCNTs have aligned in the PP matrix under HEF, which corresponds to Figure 3A and B. However, the difference increases from 1 to 2 wt.%, indicating the effectiveness of HEF in increasing the conductivity of composites in this range of the MWCNT content. The σ of 1 wt.% MWCNTs is close to that of untreated PP/MWCNT composites with 2 wt.% MWCNTs. The σ of 2 wt.% MWCNTs has a sharp rise by two orders of magnitude. At even higher concentrations, the σ of composites still increases to some extent after the effect of HEF, but the range of increase is basically kept at one order of magnitude.

According to the classical percolation theory [20], the relationship between the conductivity (σ_m) of a polymer filled with conductive particles and the mass fraction (m) of the particles in the mixture above the percolation threshold mass fraction (m_c) can be expressed according to Eq. (1):

$$\sigma_m = \sigma_0 (m - m_c)^t \tag{1}$$

where σ_0 is the conductivity of the conductive filler and t is the critical exponent related to the dimensionality of the system. As shown in Figure 5 (inset), the best linear-fitted log σ_m vs. log $(m-m_c)$ plot was created using Eq. (1) by considering the value for $\varphi_c \approx 2.42\%$ (untreated) and 1.68% (HEF), and the critical exponent (t) was calculated and found to be $\approx 1.79 \pm 0.3$ (untreated) and 2.56 ± 0.24 (HEF) from the slope of log σ_m vs. log $(m-m_c)$ plot. That is, the percolation threshold was reduced from 2.42 to 1.68 wt.% under the effect of HEF on the melt processing of PP/MWCNT composites.

3.3 Dielectric properties

From the percolation power law [21], when the volume fraction of the conductor is slightly lower than the percolation threshold, the dielectric constant of the composite will have a remarkable growth:

$$\varepsilon = \varepsilon_0 \left| \frac{f_c - f_{CNT}}{f_c} \right|^{-q} \tag{2}$$

where ε and ε_0 are the dielectric permittivity of the composite and polymer matrix, respectively, f_{CNT} is the volume fraction of MWCNTs, f_c is the percolation threshold, and q is a critical exponent equal to 1.0. When the content of the filling conductor is equal to or higher than the percolation threshold, the composites will change from insulator to conductor and the dielectric properties of materials will disappear.

The dielectric performance of the PP or PP/MWCNTs with and without the applied HEF is shown in Figure 6. As we can see, dielectric permittivity increases with the loading of MWCNT increase. The increase of ε in the polymer composites with the introduction of conductive particles was based on the enhancement of interfacial polarization. MWCNTs effectively increased ε, especially near the percolation threshold of the MWCNT concentration. Tan δ, however, also increased simultaneously.

With applied HEF, the dielectric performance of PP/MWCNTs has a considerable and interesting change, especially in 1 and 2 wt.% MWCNTs (Figure 7). In samples with 1 wt.% MWCNTs, the ε of the sample treated by HEF has a great improvement compared to the untreated sample, whereas the tan δ of the sample still remains stable at about 0.5. This is important for dielectric applications. When the MWCNT content increases to 2 wt.%, the effect of HEF also leads a dielectric permittivity lifting, but the tan δ of composites reaches a fairly high level and it cannot be used as a dielectric material. With regard to MWCNT/polymer composites, the increase in dielectric permittivity could be attributed to the interfacial polarization effect, which is ascribed to the accumulation of many charge carriers at the internal interfaces between MWCNTs and PP. In this work, it is much easier for MWCNTs to directly connect with one another and form an MWCNT network in the composites when treated by HEF than in untreated

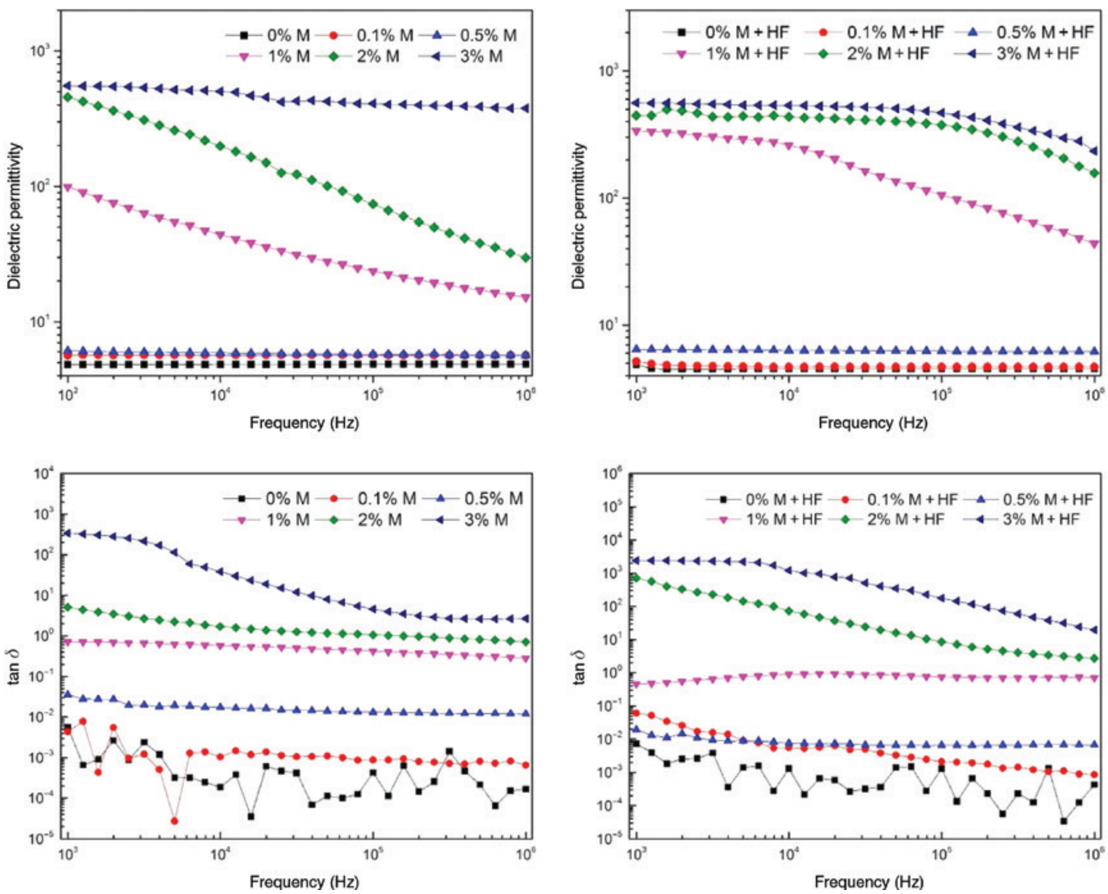

Figure 6: Dielectric performance of PP or PP/MWCNTs with and without the applied HEF.

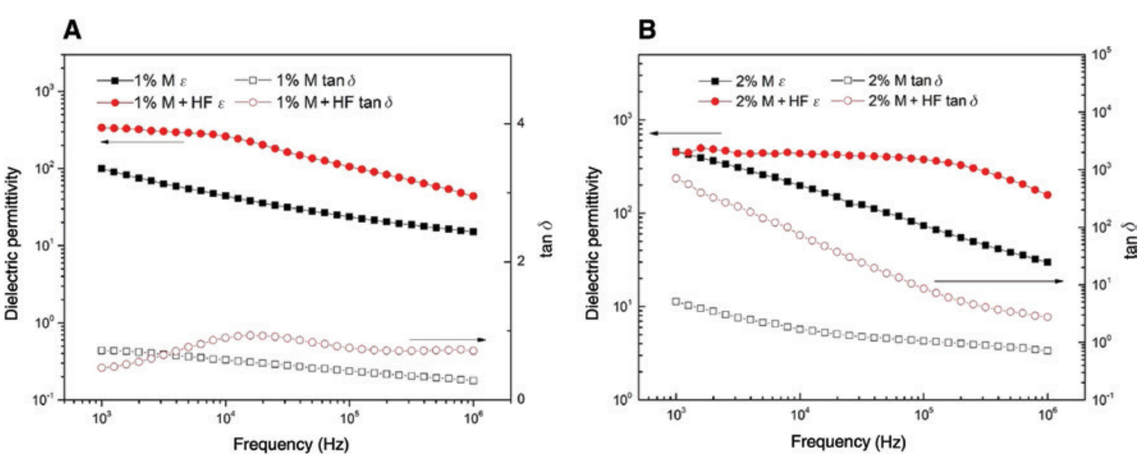

Figure 7: Effect of HEF to the dielectric performance of PP/MWCNT composites: (A) 1 wt.% and (B) 2 wt.%.

composites, as already confirmed in TEM graph and the result of the electrical conductivity measurement. Thus, at the same content of MWCNTs, the dielectric constant of HEF-treated composites is obviously higher than that of untreated composites because of the formation of the MWCNT network in HEF composites. On the contrary, the direct connection of MWCNTs in HEF composites and the smaller distance between adjacent MWCNTs leads to a high DC conductance, which contributes to a higher dielectric loss, especially in 2% MWCNTs.

3.4 Rheological properties

Owing to their high aspect ratio and specific surface area, the orientation behavior of MWCNTs in the matrix due to

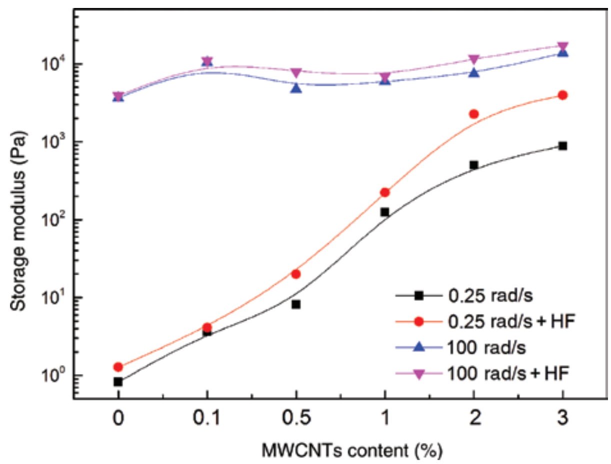

Figure 8: Storage modulus versus MWCNT content of PP/MWCNT composites with and without the applied HEF at 0.25 and 100 rad/s.

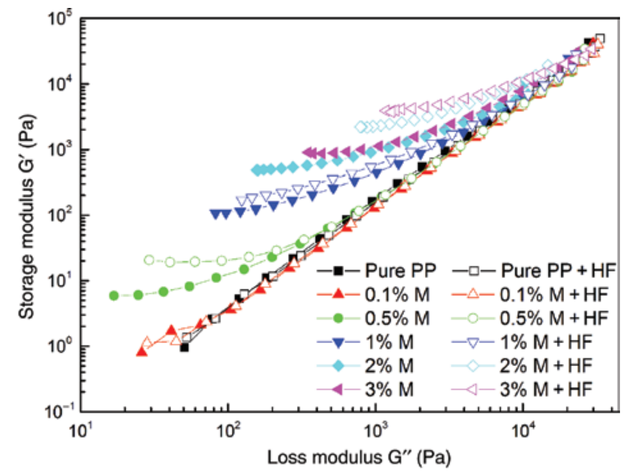

Figure 9: Storage modulus G' as a function of loss modulus G'' of PP/MWCNT composites with and without the applied HEF.

HEF is bound to affect the microstructure of composite materials and subsequently affect the rheological behavior of the composites. Therefore, through the analysis of the rheological properties of composite materials, we can further study the relationship between the alignment of MWCNTs in the matrix and the rheological properties of the composites.

The storage modulus represents the ability of viscoelastic materials to store elastic energy under loading. The storage modulus of PP/MWCNT composites with and without applied HEF is shown in Figure 8. At low frequency (0.25 rad/s), it can be seen that the more MWCNTs are added into composites, the more the storage modulus is improved, which confirms the reinforcement effect of MWCNTs on the PP composites. What's more, the storage modulus of the composites processed under the effect of HEF is larger than the composites produced without exposure to HEF. Besides, this kind of lifting effect is more obvious with the increase of the MWCNT content. However, at high frequency (100 rad/s), this is no longer the enhancement of MWCNTs to the PP matrix as well as the improvement along the direction of HEF.

The improvement on the storage modulus at relatively low frequency (0.25 rad/s) is based on the interconnection between MWCNTs and the matrix as well as the network structure formed by MWCNTs in the matrix. The shear force at low frequency is not large enough to overcome this obstacle in the flow process and the storage modulus of the composites increases macroscopically. Under the effect of HEF, the alignment of MWCNTs accelerates the formation of the MWCNT network in the matrix and thereby forms more entanglements between the network structure and the molecular chain of PP as the obstacle in the flow process. Therefore, in the same content, the storage modulus of PP/MWCNT composites with exposure to HEF is higher. However, for high frequency (100 rad/s), the network structure of MWCNTs is destroyed seriously by high loading and the reinforcement effect is no longer obvious [22]. Similar results [15] were reported previously.

Figure 9 shows a plot of the storage modulus G' versus the loss modulus G'' with frequency. Such plots were used by Han and Jinhwan [23] to investigate temperature-induced changes in the microstructure of homopolymers, block copolymers, and blends. It was proposed that if the microstructure does not change with temperature, the curves of $\log G'$ vs. $\log G''$ at different temperatures should coincide. Harrell and Nakajima [24] used $\log G'$-$\log G''$ curves to investigate the influence of the branching and molecular weight distribution width of polyethylene on its microstructure. In addition, $\log G'$-$\log G''$ curves were used to research multiphase systems and analyze the structure transformation between the matrix and the filler in systems at a given temperature. Pötschke et al. [25] used such plots to explore the rheological behavior of PP/MWCNT composites and found that the slope of G' vs. G'' decreases with increasing MWCNT content, which means the microstructure of composite changes.

For the $\log G'$-$\log G''$ curves of PP/MWCNT composites with and without the effect of HEF in Figure 9, the storage modulus G' (for a given loss modulus G'') increases significantly with the increasing content of MWCNTs. The slope of G' vs. G'' can be obtained by linear fitting and the slope of each curve is listed in Table 1. It can be clearly seen that the slope of the G' vs. G'' curve of the untreated sample is larger than the HEF sample in every MWCNT content. This interesting result indicated that the microstructure of composites is changed under the effect of HEF. This could

Table 1: Slope of the logG'-logG'' curves of PP/MWCNT composites with and without the effect of HEF.

MWCNT content (wt.%)	Untreated	HEF
0	1.623	1.589
0.1	1.541	1.53
0.5	1.198	1.159
1	0.96	0.929
2	0.707	0.647
3	0.845	0.643

be attributed to the alignment of MWCNTs in HEF forming a more perfect network structure in the PP matrix.

4 Conclusion

In this work, random and aligned MWCNT/PP composites were analyzed by applying an HEF to the composite melt at the hot-compression molding stage.

As a result of the alignment of MWCNTs, the AC electrical conductivity of PP/MWCNT composites showed a significant increase compared to the random sample. A lower percolation threshold (1.68 wt.%) was obtained in the aligned composites than in the random composites (2.42 wt.%). The dielectric measurement results indicated that the dielectric constant of both random and aligned composites increases largely with the increasing content of MWCNTs. At MWCNT contents of 1 wt.%, a high ε and a low $\tan\delta$ were obtained for the aligned composite, whereas a high ε but a high $\tan\delta$ were obtained at MWCNT contents of 2 wt.%. Moreover, the rheological analysis showed an improvement in the storage modulus of the composites due to the MWCNT alignment and the enhancement was more distinct with the increase of the MWCNT content. The difference of the slope of the logG'-logG'' curves of the composite with and without the effect of HEF revealed that the microstructure has been changed in virtue of the effect of HEF and the aligning MWCNTs.

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