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Effect of electrically inert particulate filler on electrical resistivity of polymer/multi-walled carbon nanotube composites

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ABSTRACT

Electrically conductive polypropylene (PP)/multi-walled carbon nanotube (MWCNT) composites containing electrically inert particulate filler calcium carbonate ($CaCO_3$) have been prepared in a rotational rheometer. A significant reduction in electrical resistivity was found with the addition of $CaCO_3$. The concept of effective concentration of MWCNTs is proposed to quantitatively evaluate the effect of $CaCO_3$. A master curve was achieved by plotting electrical conductivity (or resistivity) data of various composite systems, with or without $CaCO_3$, against their effective volume fraction of MWCNT, validating the concept of effective concentration. Similar results were obtained from investigations on MWCNT composite systems of different inert fillers, including talc and wollastonite, and host polymers, such as polyoxymethylene and polyamide, demonstrating the generality of the present observation.

1. Introduction

Carbon nanotubes (CNTs) have intrigued tremendous interests in scientific research ever since the landmark work of Iijima published in 1991 [1]. Because of their outstanding electrical and physical properties [2,3], many applications have been proposed, including conductive and high-strength composites [4,5], antistatic film and electromagnetic shielding materials [6–8]. Compared to traditional conductive fillers such as carbon blacks and carbon fibers, one of the main advantages of using CNTs is the significant reduction in percolation threshold. For carbon black-filled polymers, the percolation thresholds are usually up to 5–20 wt% [9]; and for carbon fiber-filled polymers the percolation thresholds are in the range of 9–18 wt% [10,11]. However, much lower percolation thresholds have been reported for CNT-filled polymers. For example, a percolation threshold of 1–2 wt% was found for polypropylene (PP)/multi-walled carbon nanotube (MWCNT) composites prepared by melt mixing [12], and even lower percolation concentration values reported for polycarbonate (PC)/single-walled carbon nanotube (SWCNT) composites prepared by solution method (0.11 wt%) and polyimide/SWCNT composites obtained via in-situ polymerization (0.05 vol%) [13,14].

New methods for electrical modification of polymer/CNT composites have received considerable attention recently. Grunlan et al. [15] used poly(vinyl acetate) (PVAc) emulsion to prepare PVAc/SWCNT composite films. The percolation threshold is only 0.04 wt% because the space available for SWCNTs to form conductive networks is dramatically reduced by PVAc solid particles which create excluded volume and push SWCNTs into the interstitial space [15]. Xu et al. [16] found a density–conductivity relationship for polyurethane (PU)/CNT composites, and obtained ultralight conductive PU/CNT foam. In recent years, using binary polymer blends instead of single polymers as the matrices has shown to be a good way of improving the electrical conductivity and lowering the percolation threshold. The concept of double percolation, proposed initially by Zhang et al. [17] for carbon black-filled high density polyethylene (HDPE)/isotactic polypropylene (iPP) blend, was applied to CNT-filled binary polymer blends. The blends become electrically conducting at a much lower CNT content than the corresponding homopolymers, i.e. the percolation thresholds are greatly decreased. For example, Pötschke et al. [18,19] used melt mixing to prepare MWCNT-filled co-continuous polymer blends (polyethylene/PC). The percolation threshold is only 0.41 vol%, which is much smaller than that for PC/MWCNT composites (1.0 vol%) [20].

Making polymer composites by incorporating inert fillers is an alternative to polymer blends for changing the properties of polymeric materials. Electrically inert particulate fillers such as calcium carbonate ($CaCO_3$), talc and wollastonite are commonly used in the preparation of polymer-based composites for the purpose of improving the performance [21–23]. These inorganic fillers acting as hard particles can improve significantly the moduli of the polymers and also affect crystallization process of the polymer matrices [23]. Incorporation of such fillers into CNT-filled polymers can reduce the space available for CNTs to form conductive networks and thus

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could increase the conductivity, since CNTs can not diffuse into the fillers which are solid particles. The aim of this work is to show the enhancement in electrical conductivity of CNT-filled polymers by incorporating electrically inert particulate fillers such as $CaCO_3$. A literature survey has shown that clay has been used to improve the electrical properties of conductive composites [24–26]. The role of clay was to assist dispersion of the conductive fillers and thus result in better electrical proprieties [24,25]. Pötschke et al. incorporated montmorillonite (MMT) into MWCNT-filled PC/PP blends to prevent migration of MWCNTs from PC phase to PP phase, and improvement in electrical properties of the blends was also achieved [27].

In this work, the enhancement of electrical conductivity is first demonstrated by incorporating $CaCO_3$ into MWCNT-filled PP at various MWCNT loadings. And then the inert filler, the matrix polymer and the dispersion state of MWCNTs are varied in order to show the versatility of the findings. The concept of effective concentration of MWCNTs is proposed to evaluate the effect created by the inert filler and proved valid for all the investigated polymer/MWCNT/inert filler systems.

2. Experimental

2.1. Materials

MWCNTs used in this work were supplied by Professor Wei [28] from Tsinghua University, China. The purity is above 95% in weight. The diameter of MWCNTs is ranged 3–20 nm with the statistic average diameter of 10 nm, and the length was of several micrometers. PP (S1003), polyamide 6 (PA6, 1013B) and polyoxymethylene (POM, F2002) were purchased from China SINOPEC Yanshan Chemical Corporation, UBE and Mitsubishi, respectively. $CaCO_3$ (1250 mesh), talc (1250 mesh) and wollastonite (1250 mesh) were purchased from Beijing Guoli Superfine Powder Co. Ltd.

2.2. Sample preparation

Polymer/MWCNT composites containing different amounts (0, 20 and 30 wt%) of electrically inert filler ($CaCO_3$ or talc or wollastonite) were prepared in a rotational rheometer (RM-200A Rheometer, Harbin Hapro Electrical Technology Co. Ltd) at 1, 2, 3, 4 and 5 wt% MWCNT loadings. The screw speed was set to 60 rpm and the mixing time was 10 min. The mixing temperatures were 250, 180 and 250 °C for PP, POM and PA6, respectively.

PP/MWCNT/$CaCO_3$ composites were also prepared with a self-made small scale melt mixing equipment at 1, 2, 3, 4 and 5 wt% MWCNT loadings under similar conditions. The equipment is specially designed for melt mixing of small scale (1–4 g) polymeric materials. It consists of two parts: the mixing part which contains a barrel and a screw, and the control part which adjusts the mixing temperature and the rotating speed of the screw.

2.3. Measurements

Prior to the electrical resistivity measurements, the composites were compressed into plates under a pressure of 8 MPa for 5 min using a hot-press at temperatures of 230, 210 and 290 °C for PP, POM and PA6, respectively. Disk samples with a diameter of 30 mm and thickness of 2.5 mm or diameter of 75 mm and thickness of 0.38 mm were prepared for low and high resistivity measurements, respectively.

Samples with electrical resistivity higher than $10^8\,\Omega$ cm were measured by ZC-36 Resistivity Test (Shanghai Cany Precision Instrument Co., Ltd). The principle of the test is based on the formula: $\rho_v = ((R_v \cdot \pi d^2)/4 \cdot L)$, where L is the thickness of the sample (0.38 mm), d is the diameter, and R_v is the measured volume resistance [28]. For more conductive samples (lower than $10^8\,\Omega$ cm), the electrical resistivity was measured using a four-point test fixture (i.e. silver wire was used as electrode material and silver paint was used to ensure good contact of the sample surface with the electrodes to reduce the contact resistance). Data from four measurements were averaged.

Field emission scanning electron microscopy (FESEM) was performed on a JEOL model JSM-7401 apparatus with an operating voltage of 1.0 kV to investigate the dispersion of MWCNTs of the cryo-fractured surfaces of the composites.

3. Results and discussion

3.1. Electrical resistivity and percolation in PP/MWCNT/$CaCO_3$ composites

The influence of $CaCO_3$ on the electrical resistivity of the PP/MWCNT composites prepared by rotational rheometer at various MWCNT loadings is shown in Fig. 1a. The curve of PP/MWCNT composites without $CaCO_3$ shows a percolation threshold at 1–2 wt% of MWCNT loading, which is in agreement with the one reported by Seo and Park [12] for PP/MWCNT composites prepared by melt mixing, although Andrews et al. [29] have reported a much lower value of 0.10 wt% (0.05 vol%) due to presumably much better

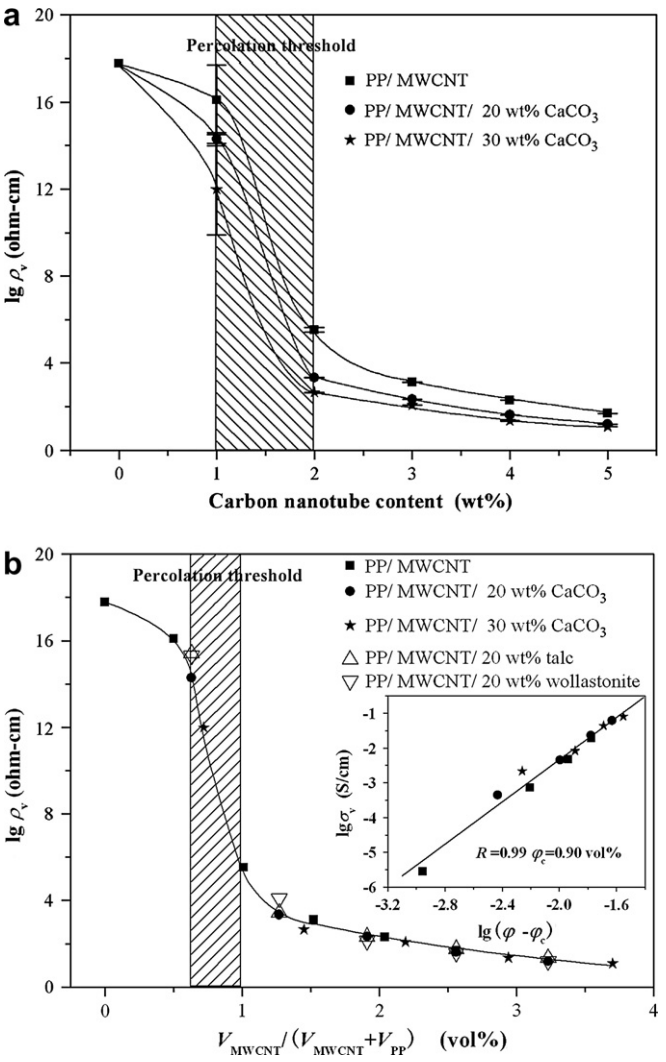

Fig. 1. (a) The influence of $CaCO_3$ on the electrical resistivity of PP/MWCNT composites and (b) electrical resistivity–effective concentration curve of PP/MWCNT/$CaCO_3$ composites.

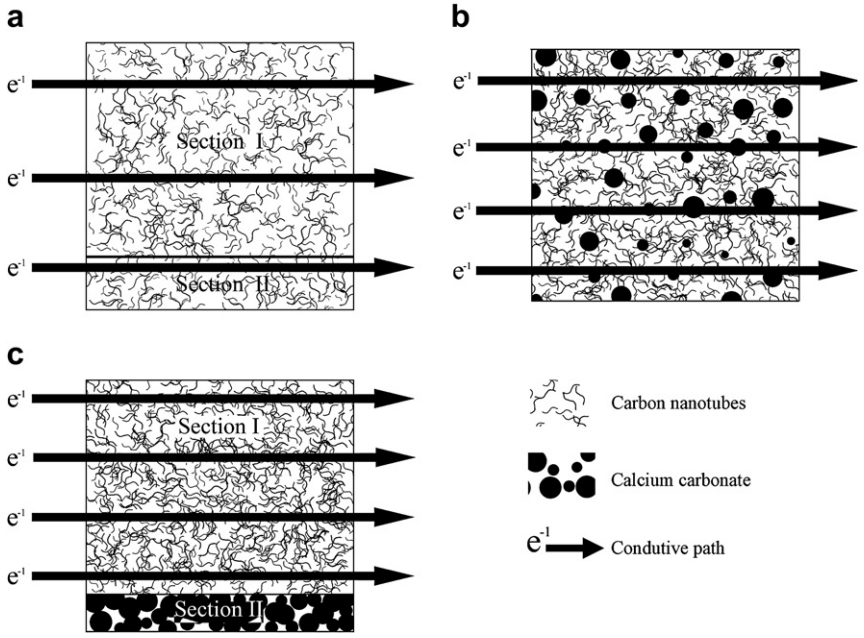

Fig. 2. Illustration of the influence of $CaCO_3$ on the resistivity of PP/MWCNT composite: (a) PP/MWCNT composite without $CaCO_3$, (b) PP/MWCNT/$CaCO_3$ composite, real state, and (c) PP/MWCNT/$CaCO_3$ composite, imaginary state.

dispersion of MWCNTs in PP. After incorporation of 20 wt% $CaCO_3$, the electrical resistivity decreases significantly at all the investigated MWCNT loadings, especially at 2 wt% MWCNT loading where a decrease of two orders of magnitude is observed. The electrical resistivity decreases further when the content of $CaCO_3$ is increased to 30 wt%. This phenomenon can be illustrated in Fig. 2. In PP/WMCNT composite, the electrons pass through the composite by the conductive network formed by MWCNTs (Fig. 2a). After incorporation of $CaCO_3$ into the PP/WMCNT composite, $CaCO_3$ will hold up certain space, so MWCNTs can connect with each other in a higher probability, which will facilitate the electron pass through the composite more easily (Fig. 2b), thus the electrical resistivity of the composite decreases. In order to show this more clearly, the real state (Fig. 2b) of PP/MWCNT/$CaCO_3$ composite can be assumed to be the imaginary state as shown in Fig. 2c, where section II consists of $CaCO_3$ only. Since $CaCO_3$ exists in the form of solid particles (Fig. 2c, section II), MWCNTs can not diffuse into $CaCO_3$, but can only diffuse into PP, i.e. the conductive path can only be built up in the PP phase (Fig. 2c, section I). Also, because the electrical resistivity of PP/30 wt% $CaCO_3$ is very similar to that of PP ($\log_{10}\rho_v = 17.0$ compared to 17.7), $CaCO_3$ can be considered electrically inert and thus does not contribute to the formation of the conductive path. In Fig. 2c, the resistivity of the composite depends on the volume fraction of MWCNTs to PP (section I), rather than the volume fraction of MWCNTs to the whole composite (sections I and II). Therefore, the electrical resistivity is decreased after incorporation of $CaCO_3$ as a result of the increase in MWCNT/PP proportion at the same MWCNT loading (Fig. 2a and c).

Based on the above discussion, the concept of effective concentration of MWCNTs is proposed in order to quantitatively

Table 1
The effect of $CaCO_3$ content on the effective concentration and percolation concentration

$CaCO_3$ content (wt%)	Increase in effective concentration (%)	φ_c (vol%)
0	0	0.90
20	25.0	0.72
30	42.9	0.63

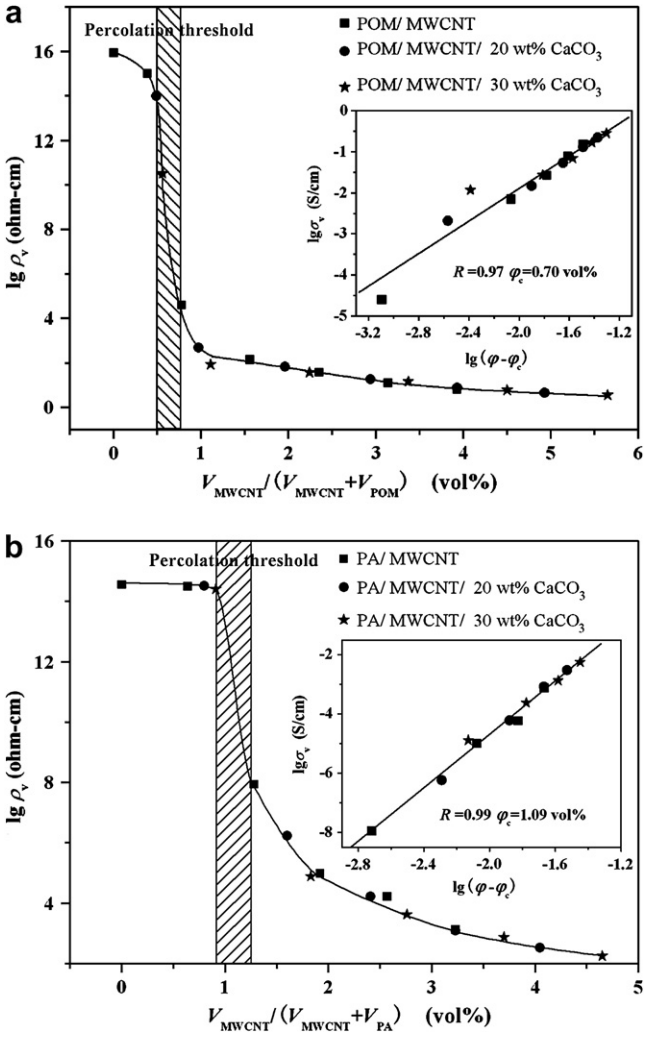

Fig. 3. Electrical resistivity–effective concentration curve of (a) POM/MWCNT/$CaCO_3$ composites and (b) PA6/MWCNT/$CaCO_3$ composites.

evaluate the effect of calcium carbonate. Thus, the effective concentration of MWCNTs is defined as the volume of MWCNTs to the sum of the volume of MWCNTs and the polymer:

$$V_{\mathrm{MWCNT}}/\left(V_{\mathrm{MWCNT}}+V_{\mathrm{polymer}}\right)$$

where V_{MWCNT}: volume of the MWCNTs and V_{polymer}: volume of the polymer matrix.

The effective concentrations of MWCNTs for all the data shown in Fig. 1a are calculated. When the electrical resistivity data are plotted against effective concentrations of MWCNTs, as shown in Fig. 1b, the three curves in Fig. 1a combine into one master curve which is the one without $CaCO_3$, proving the validity of the concept of effective concentration of MWCNTs. When $CaCO_3$ is incorporated into PP/MWCNT composites, the effective concentration of MWCNTs increases and the electrical resistivity is reduced accordingly.

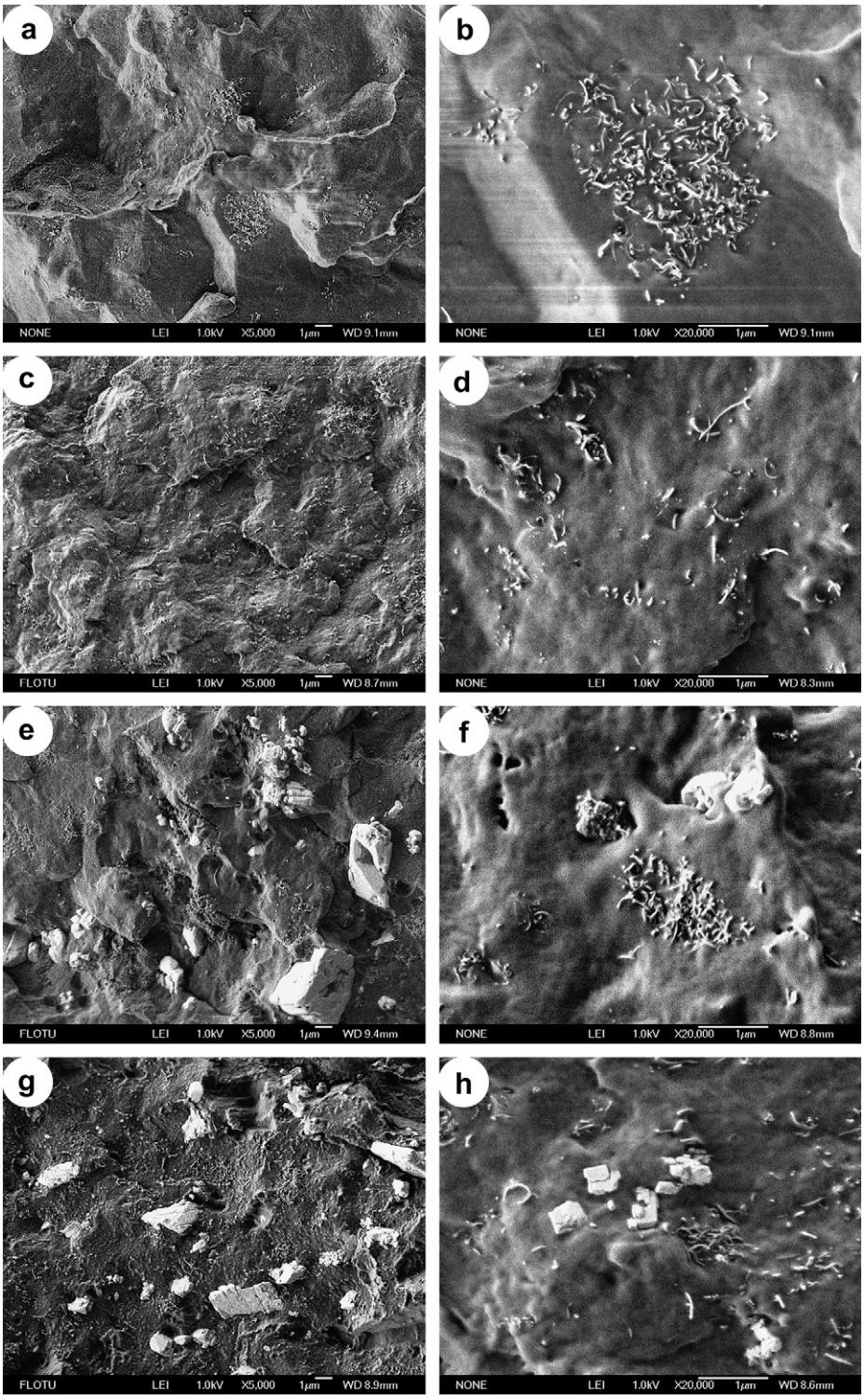

Fig. 4. FESEM pictures showing dispersion state of MWCNTs at two different magnifications: PP/5 wt% MWCNT composites prepared by (a and b) self-made equipment and (c and d) rotational rheometer; PP/5 wt% MWCNT/20 wt% $CaCO_3$ composites prepared by (e and f) self-made equipment and (g and h) rotational rheometer.

According to the percolation theory, the dependence of electrical resistivity data on the conductive filler content follows the power law: $\sigma_{DC} = \sigma_0(\varphi - \varphi_c)^t$ [30], when the conductive filler volume concentration (φ) is above the critical volume fraction (φ_c). The inset in Fig. 1b shows the fitting curve with a correlation factor $R = 0.99$ from our experimental data (squares, dots and stars). The fitting parameters are obtained in terms of φ_c (0.90 vol%) and critical exponent t (2.80). As shown in Table 1, when 20 wt% of $CaCO_3$ is added to PP/MWCNT composites, the effective concentration of MWCNTs increases by about 25%, and thus the real MWCNT loading decreases by 20%, i.e. the real MWCNT loading is only 0.72 vol% at φ_c (0.90 vol%). A decrease in MWCNT loading at the percolation threshold is clearly evidenced with the use of $CaCO_3$. The more $CaCO_3$ is used, the more reduction in MWCNT loading is seen.

In order to demonstrate the versatility of the electrical resistivity–effective concentration of MWCNT curve in terms of electrically inert particulate filler, $CaCO_3$ is changed into talc and wollastonite. The data are shown in Fig. 1b as triangle (△) and inverse triangle (▽), and are all on or around the curve with little deviation, revealing that the type of the electrically inert particulate filler is of little importance in view of the electrical resistivity of the composites. Although different inert fillers have different size, shape and density, their effect on the values of electrical resistivity is the same, because the effective concentration is the same as long as the inert fillers are of the same weight (by design the total weight of the composite is kept constant).

3.2. Percolation in POM/MWCNT/$CaCO_3$ and PA6/MWCNT/$CaCO_3$ composites

In order to demonstrate the validity of the concept of effective concentration of MWCNTs in view of the polymer matrix, PP is substituted by POM and PA6, and $CaCO_3$ is used as the electrically inert filler. Thus, POM/MWCNT and PA6/MWCNT composites containing 0, 20 and 30 wt% of $CaCO_3$ at various MWCNT loadings were prepared, and the electrical resistivity data are plotted against effective concentrations of MWCNTs. The curves are shown in Fig. 3. One master curve can be drawn for each system with only little deviation, proving the general applicability of the concept of effective concentration of MWCNTs. The curves fitting the power law are shown in the insets of Fig. 3. The calculated φ_c values are 0.70 and 1.09 vol% for POM/MWCNT/CaCO3 and PA6/MWCNT/$CaCO_3$ composites, respectively. The latter is much lower than that found in the literature [31] for PA6/MWCNT composites (4–6 wt%) probably due to better dispersion of MWCNTs in PA6. The φ_c values of PP/MWCNT, POM/MWCNT and PA/MWCNT composites are 0.90, 0.70 and 1.09 vol%, respectively. The difference among the values may be caused by several factors such as polymer processing viscosity, surface tension, polarity and crystallization [32,33].

3.3. Effect of MWCNT dispersion on electrical resistivity of PP/MWCNT/$CaCO_3$ composites

As shown in previous studies found in the literature [34–36], the dispersion state of CNTs has a significant influence on the electrical resistivity and percolation threshold of CNT-filled polymers. Different mixing tool could give different dispersion, and thus different electrical resistivity–MWCNT concentration curve. In order to show applicability of the concept of effective concentration of MWCNTs in view of different dispersion state of MWCNTs (i.e. different mixing tool), a self-made small scale melt mixing equipment was also used to prepare MWCNT-filled PP containing 0, 20 and 30 wt% of $CaCO_3$ at various MWCNT loadings. The dispersion of MWCNTs is investigated by FESEM and compared with that observed with the rotational rheometer (Fig. 4). The dispersion of

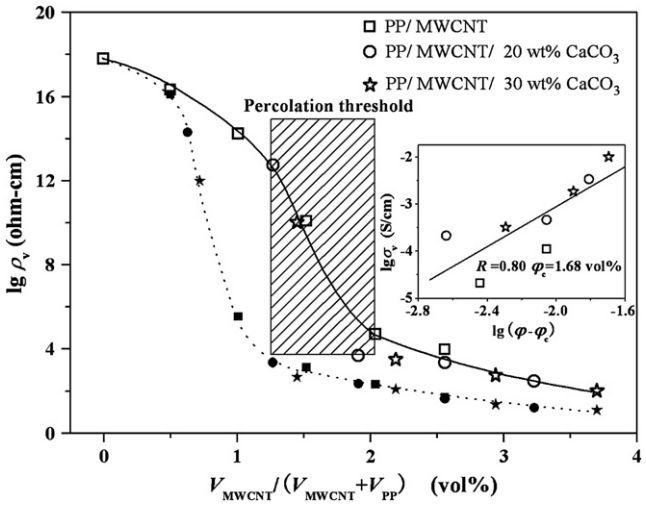

Fig. 5. Electrical resistivity–effective concentration curve of PP/MWCNT/$CaCO_3$ composites prepared by self-made equipment.

MWCNTs in PP with the self-made equipment (Fig. 4a and b) is clearly worse than that with the rotational rheometer (Fig. 4c and d). In the former case, individual MWCNT can hardly be seen, and big agglomerates with a size of about 3 μm are observed. However, in the latter case, individual MWCNT is present and the size of the agglomerates is considerately smaller. When $CaCO_3$ is incorporated into MWCNT-filled PP, the dispersion state of MWCNTs in both cases is almost unchanged (Fig. 4e–h), indicating that the presence of $CaCO_3$ in the composites does not change the dispersion state of MWCNTs. $CaCO_3$ is observed as irregular micrometer particles, and its dispersion state is similar in the two cases.

The electrical resistivity data are plotted against effective concentrations of MWCNTs in Fig. 5 for PP/MWCNT/$CaCO_3$ composites prepared by self-made mixing equipment (unfilled symbols). The data points have little deviation to the curve, revealing the validity of the concept of effective concentration in this case. The curve fitting the power law is shown in the inset of Fig. 5. The calculated φ_c value is 1.68 vol%, which is higher than that obtained with the rotational rheometer (filled symbols, 0.90 vol%). The curve for the same type of composite prepared by rotational rheometer is shown as broken line for comparison. The difference between the two curves is obvious. The curve obtained with the self-made equipment is well above the one obtained with the rotational rheometer, meaning higher electrical resistivity with the self-made equipment at all the effective concentrations of MWCNTs due to worse dispersion of MWCNTs mentioned above. From the two curves shown in Fig. 5, it can be concluded that the concept of effective concentration is applicable regardless of the dispersion state of MWCNTs, i.e. the electrical resistivity–effective concentration of MWCNT curve can be drawn as long as the data are obtained under the same processing conditions.

4. Conclusions

Electrically inert particulate fillers can be used for electrical modification of polymer/MWCNT composites. Incorporation of such fillers into polymer/MWCNT can significantly lower the electrical resistivity and percolation threshold of the materials. The concept of effective concentration of MWCNTs is proposed to quantitatively evaluate the effect of electrically inert fillers on the electrical resistivity of the materials. The electrical resistivity–effective concentration curve showing electrical percolation can be plotted using data obtained with and without $CaCO_3$ at various

MWCNT loadings. The concept of effective concentration is generally applicable to different types of inert fillers, polymer matrices and dispersion state of MWCNTs. The method reported here is a viable alternative to the existing electrical modification methods.

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