

Conductive Network Formation and Electrical Properties of Poly(vinylidene fluoride)/Multiwalled Carbon Nanotube Composites: Percolation and Dynamic Percolation

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ABSTRACT: Conductive network formation and its dynamic process for multiwalled carbon nanotubes (MWNTs) and carboxyl-tethered MWNT (MWNT-COOH) filled poly(vinylidene fluoride)(PVDF) systems were investigated. Based on real-time tracing the variation of electrical resistivity of systems with isothermal treatment time, the conductive network formation was evaluated. It was found that the conductive network formation was temperature and time dependent. The percolation time, characterized at a certain annealing time where the electrical resistivity started to decrease drastically, decreased with the increase of the filler concentration or the annealing temperature. However, the values of the percolation time and the activation energy of conductive network for-

mation for the PVDF/MWNT-COOH system were higher than those of the PVDF/MWNT system, indicating that the interaction between MWNTs and PVDF molecules played an important role in the conductive network formation of the composites. Furthermore, a modified thermodynamic percolation model was proposed to predict the percolation time of PVDF/MWNT composites. It was found that the calculated results fit the experimental data very well. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1405–1411, 2009

Key words: multiwalled carbon nanotubes; dynamic percolation; poly(vinylidene fluoride); conductive network; electrical resistivity

INTRODUCTION

As well known, a promising electrically conductive material can be achieved by adding only a low loading of carbon nanotubes (CNTs) in a polymer matrix owing to the high aspect ratio and the excellent electrical properties of CNTs.^{1–9} Also, improved electrical and mechanical properties of polymer/CNT composites make them as competitive candidates for many electronics application, such as Electro Magnetic Interference (EMI) shielding, electrostatic charge dissipation, antistatic charge dissipation applications etc.¹⁰

To understand the mechanism of conductive network formation in the composites, the concept “percolation” has been used to describe the critical point that starting a sharp decrease of electrical resistivity with the increase of filler content.^{5,11,12} The critical filler concentration is called the percolation threshold (ϕ_p). However, many studies revealed that not only the loading amount of the filler but also the post-treatment of the samples play an important role in an efficient conductive material.^{11–13} It had been known that the ϕ_p was greatly influenced by the melt viscosity of the polymer matrix, and the preparation conditions such as the molding time and temperature,^{14,15} indicating that conductive particles in a polymer matrix actually need time to move and congregate to form a conductive network. The previous studies showed that for the composites with a conductive filler concentration lower than the percolation threshold, the electrical resistivity decreased sharply at a critical time when the sample was annealed at a temperature higher than the melting point of the polymer matrix, suggesting that conductive particles filled polymer composites had to be regarded as thermodynamic nonequilibrium systems.^{16–20} This phenomenon was named as dynamic

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percolation, and the critical point of time known as the percolation time t_p .

Recently, more attention has been given to the dynamic percolation phenomenon of carbon black (CB) filled polymer composites.^{16–24} The dynamic percolation measurement has been considered as an effective tool to real-time monitor of the mobility of CB particles in the polymer melt because it can trace the growth of CB conductive network construction. Wu et al.^{16–18} used CB as a self-diagnostic probe to trace polymer dynamics in Poly(methyl methacrylate)(PMMA)/CB composites and found that the activation energy of the percolation time was close to the activation energy of the zero-shear-rate viscosity of the polymer. Tai et al.^{23,24} developed an approach to obtain a one-dimensional conductive composite based on the dynamic percolation and electric-field induced alignment of CB particles in low-density polyethylene (LDPE) matrix. In the previous work,¹⁹ a modified thermodynamic percolation model was also deduced to predict the percolation time for vapor-grown carbon fiber (VGCF) filled high-density polyethylene (HDPE)/isotactic polypropylene (iPP) blends.

Compared with singlewalled carbon nanotubes (SMNTs), multiwalled carbon nanotubes (MWNTs) are being studied much more extensively as the conductive filler in various fields because of their good conductivity, excellent toughness, and acceptable price,^{1,3,25} which makes common thermoplastics consisting of MWNTs as high performance materials possible. As a polymer matrix, PVDF has also attracted much attention because of its potential applications in high pyroelectric, piezoelectric, and ferroelectric materials. However, there have been few reports dealing with the dynamic percolation in MWNT-filled polymer systems up to our knowledge. In this study, the electrical properties of PVDF/MWNT composites and the growth of MWNT conductive networks in the PVDF melt were investigated by recording the variation of electrical resistivity with the treatment time. Moreover, carboxyl-tethered MWNT (MWNT-COOH) was also applied to find out how the surface properties of the filler affect the conductive network formation and the electrical properties of the composites.

EXPERIMENTAL

Materials and sample preparation

Poly(vinylidene fluoride) (PVDF) (FR 901, inherent viscosity 8 ml/g) was purchased from Shanghai 3F Company. Multiwalled carbon nanotubes (MWNTs) and carboxyl-tethered MWNTs (MWNT-COOH; content of carboxyl group is 1.23 wt %), synthesized by CVD technique, were provided by the Chengdu

Organic Chemistry, Chinese Academy of Science (Chengdu, China), with a diameter of 20–30 nm and a length of 10–30 μm . The polymer was first melted in a Haake Rheomix R600 at 190°C for 5 min, followed by addition of the MWNTs into the polymer and mixing for 15 min. PVDF and MWNTs were dried at 80°C for 24 h under vacuum before use. The samples were then melted at 190°C for 2 min, compressed under a pressure of 15 MPa for 3 min, and finally cooled at a cooling rate of 50°C/min to obtain the sheets with a thickness of 1.5 mm.

Measurements

The room-temperature electrical resistivity was measured in the thickness direction of the composite films with a KEITHLEY 6517 PICOAMMETER/VOLTAGE SOURCE. To trace the conductive network formation in the PVDF melt, the variation of resistivity with time was measured with a GZ-1 picoammeter equipped with a direct current voltage source when the composites were annealed at a given temperature above the melting point of PVDF. Specimens with the diameter of 30 mm were cut from the center area of the molded sheet and were fixed between two parallel copper electrodes. Nitrogen gas was introduced during measurement to prevent oxidation of the samples. The applied voltage for the measurement was 1 V. The variation of the electrical resistivity over the annealing time was recorded by a computer and the time interval was 5 s.

The morphologies of the samples were observed by a Hitachi S-4700 scanning electron microscope. The as-prepared specimens were broken off in liquid nitrogen and coated with an ultrathin platinum (Pt) film before observation.

RESULTS AND DISCUSSION

Figure 1 shows the variation of the room temperature resistivity with filler content for MWNT and MWNT-COOH filled PVDF composites. As the filler content increases, both PVDF/MWNT and PVDF/MWNT-COOH system exhibit a drastic transition from an electrical insulator to a conductor due to the conductive network formation. This phenomenon is called percolation, and the critical filler content is named percolation threshold (ϕ_p). It was found that the ϕ_p for the PVDF/MWNT system was about 1.62 wt %, whereas for the PVDF/MWNT-COOH system, ϕ_p was about 2.44 wt %. A higher percolation threshold for the PVDF/MWNT-COOH system can be understood based on thermodynamic considerations. Generally, incorporating carbon fillers into a polymer matrix will inevitably increase the system energy due to the incompatibility between them. Miyasaka et al.²⁶ proposed that when the total

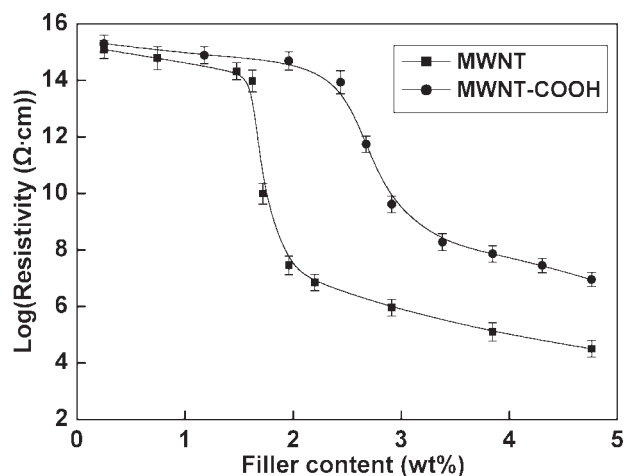


Figure 1 Filler content dependency of the room temperature resistivity for PVDF/MWNT and PVDF/MWNT-COOH.

interfacial energy, Δg , between filler particles and the polymer matrix reaches a “universal value,” Δg^* , the filler particles begin to coagulate to form the conductive network so as to avoid any further increase in the system energy, that is to say, percolation occurs. The presence of carboxyl groups enables the MWNT-COOH to act cooperatively with PVDF mol-

ecules by the hydrogen bonding, resulting in the decrease of the interfacial free energy between MWNT-COOH and PVDF molecules.

Figure 2 shows the SEM images of MWNTs, the fractured surfaces of the PVDF/MWNT and PVDF/MWNT-COOH composites. It is clearly visible that the dispersion of MWNT-COOH in the polymer matrix is relatively uniform while pristine MWNTs form many large aggregates under the same processing conditions. The better dispersion of the MWNT-COOH in PVDF matrix is due to the presence of the functional group ($-\text{COOH}$) which led to a better compatibility with PVDF.²⁷

For a filled thermoplastic system, there is always a difference in the interfacial energy between the filler and the polymer matrix. So, the filler particles will inexorably tend to coagulate together to form a three-dimensional network during the further processing. When the composites are treated isothermally at a temperature above the melting point of the polymer matrix, this process can be real-time traced by recording the variation of electrical resistivity with annealing time. To study the conductive network formation by the dynamic percolation measurement, the selected filler concentration should be lower than the percolation threshold of the composites (see Fig. 1). Figure 3(a,b) shows the time

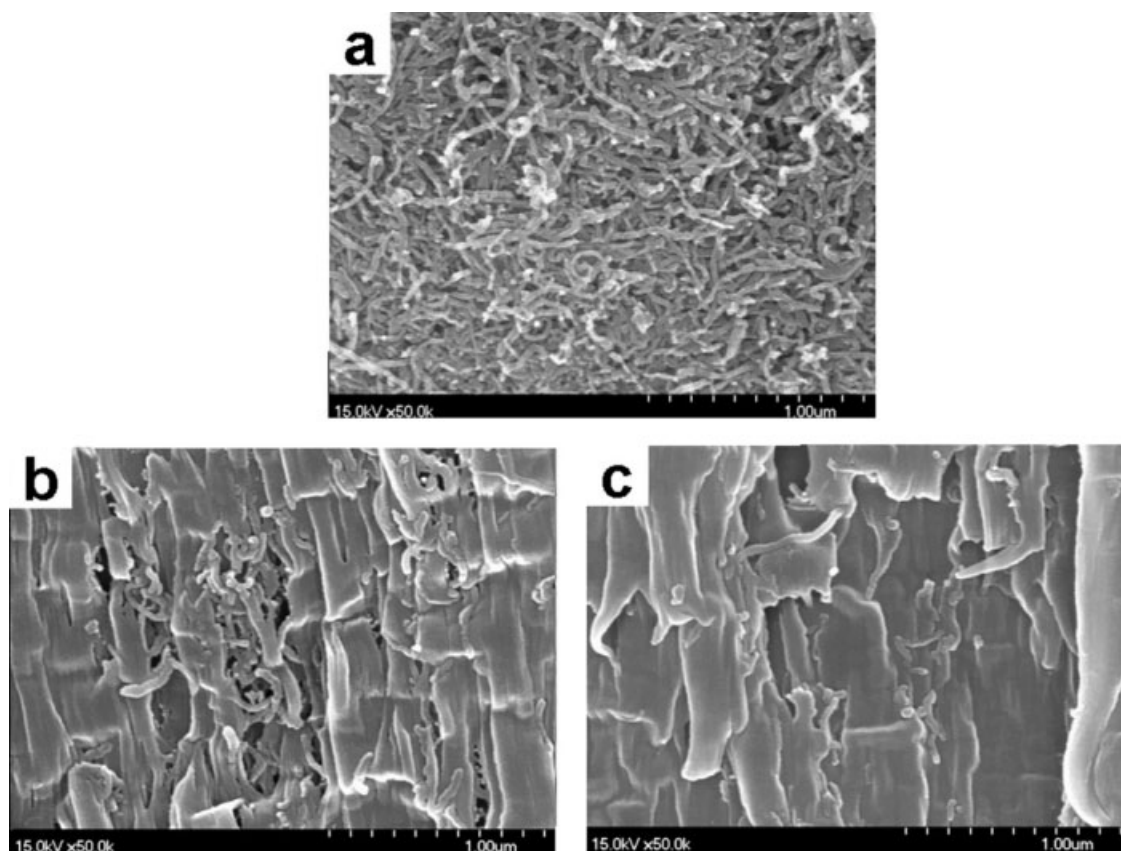


Figure 2 SEM micrographs of (a) MWNTs; (b) PVDF/MWNT (2.5 wt %) and (c) PVDF/MWNT-COOH (2.5 wt %).

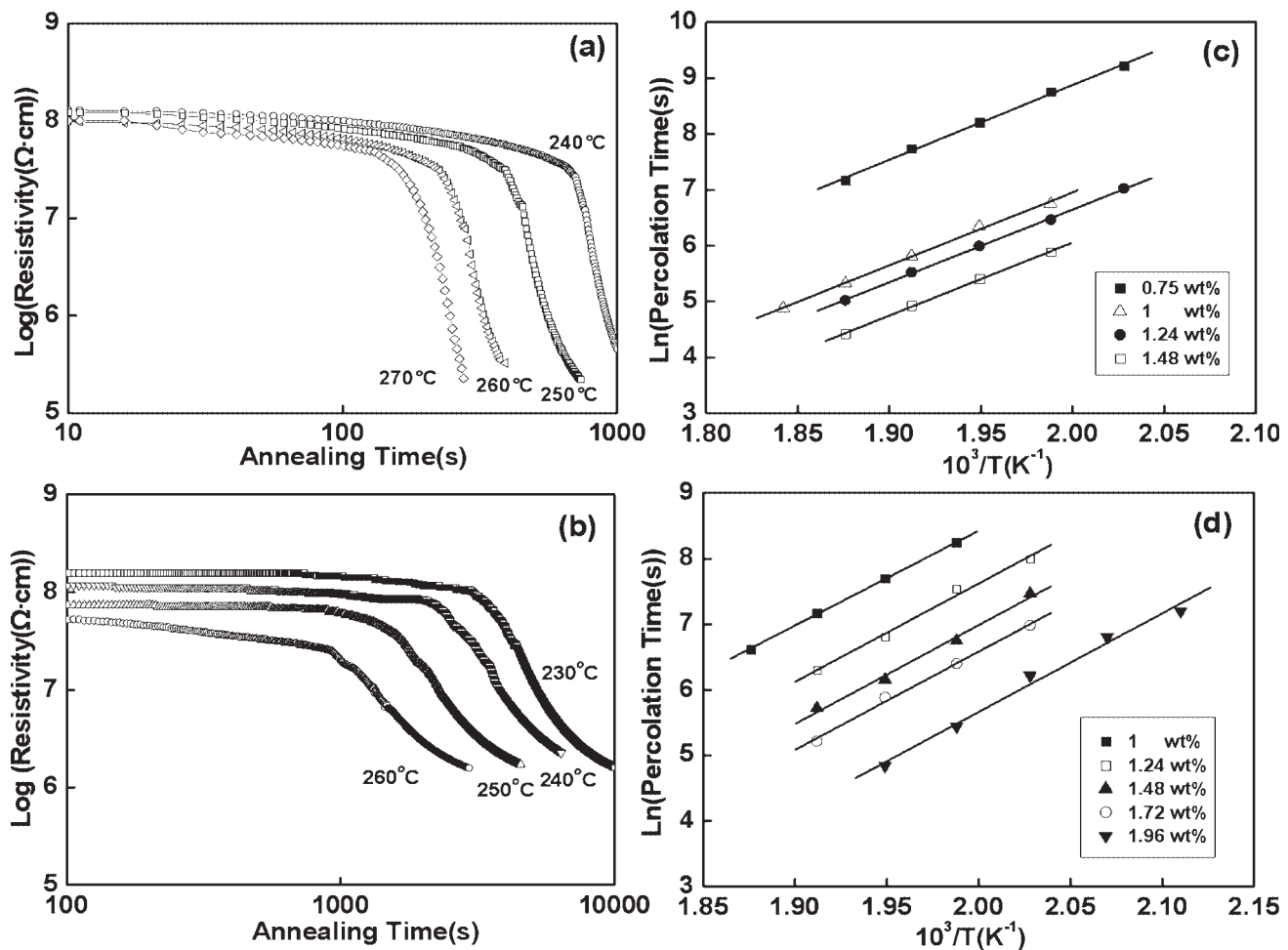


Figure 3 Dynamic percolation curves of (a) PVDF/MWNT and (b) PVDF/MWNT-COOH at various temperatures; Arrhenius plots of t_p versus the inverse of the temperature for (c) PVDF/MWNT and (d) PVDF/MWNT-COOH containing various filler contents.

dependency of resistivity for PVDF/MWNT and PVDF/MWNT-COOH under various annealing temperatures. The electrical resistivity of the composites decreases slightly as the annealing time increases in the first stage, and then decreases drastically while reaching a critical time, i.e., the transition from an insulator to a conductor. The critical annealing time is defined as "percolation time," t_p , which can be used to estimate the difficulty of the conductive network formation.

For the composite with a low filler loading, the electron hopping mechanism has been adopted to describe the electrical conductivity of the polymer/CNT composites.^{28,29} This mechanism requires the close proximity (<5 nm) of nanotubes or nanotube bundles in the composites and the direct nanotube contact is unnecessary. In this study, MWNTs coagulate together through Brownian motion during the isothermal treatment. Finally, MWNTs contact with each other or are close enough to allow the carriers hopping between MWNTs by tunneling to form a

continuous conducting mesh, resulting in a drastic decrease in the electrical resistivity. The interfacial free energy of the PVDF/MWNT system will be reduced because of the coagulation of MWNTs during the annealing, resulting in a decrease in the total free energy of the system. Therefore, the conductive network formed in the system reaches the thermodynamic equilibrium gradually.

Moreover, a shorter percolation time was observed when the annealing temperature increases. This is reasonable that the increase in the annealing temperature accelerates both the relaxation of PVDF macromolecules and the Brownian motion of MWNTs, resulting in an increase in the assembly speed of MWNTs and decreases in the viscosity resistance of the polymer melt, respectively.

Figure 3 also shows that the shape of the dynamic percolation curves does not change with increasing annealing temperature. The self-similarity of the dynamic percolation curves indicates that the primary mechanism of the conductive network

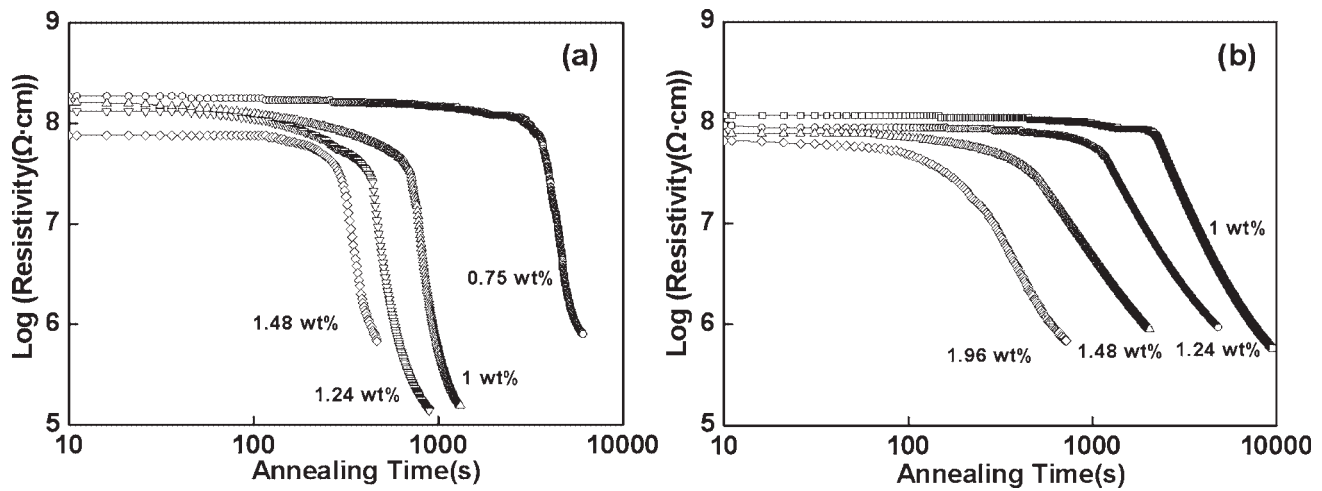


Figure 4 Dynamic percolation curves of (a) PVDF/MWNT and (b) PVDF/MWNT-COOH annealed at 240°C.

formation in the composite does not change while changing the annealing temperature. Figure 3(c,d) present the Arrhenius plots of t_p versus the inverse of the annealing temperature for PVDF/MWNT and PVDF/MWNT-COOH, respectively. A parallel linear relationship family series is observed for various MWNT contents. From these plots, the activation

energy of the conductive network formation can be calculated using eq. (1):²²

$$\ln(t_p) = \ln A - E_a/RT \quad (1)$$

where E_a is the activation energy, R is the gas constant, and T is the absolute temperature. The value

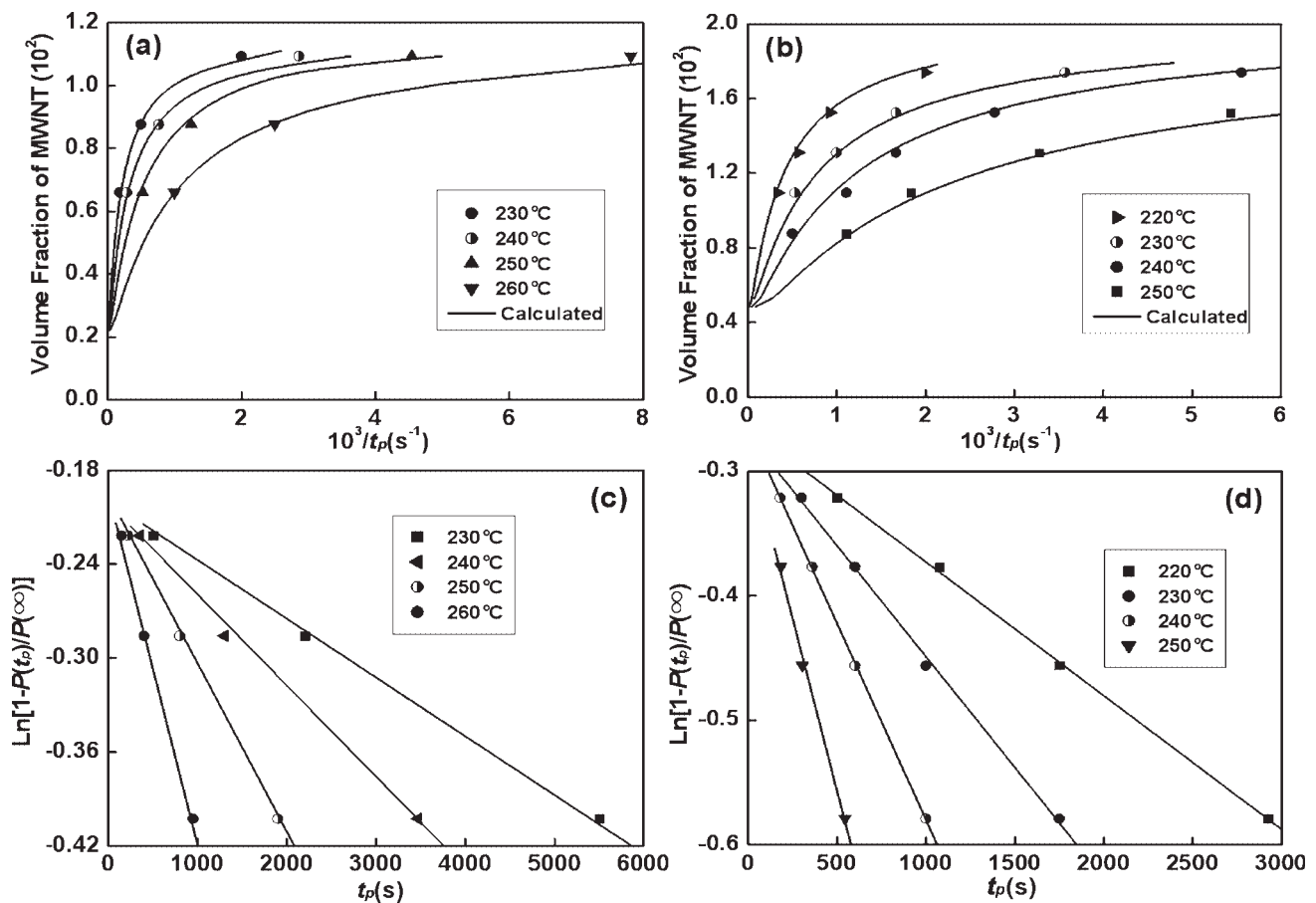


Figure 5 Plots of filler volume fraction in the matrix versus $1/t_p$ for (a) PVDF/MWNT and (b) PVDF/MWNT-COOH; Plots of $\ln[1-P(t_p)/P(\infty)]$ versus t_p for (c) PVDF/MWNT and (d) PVDF/MWNT-COOH, annealed at various temperatures.

of the activation energy is calculated to be about 125 kJ/mol for the PVDF/ MWNT-COOH system, which is much higher than that (108 kJ/mol) for the PVDF/MWNT system. This can be understood on the basis of the kinetic difficulties of the conductive network formation due to the stronger interaction between MWNT-COOH and PVDF molecules.^{16,30} A similar result was also reported by Wu et al. in the PMMA/CB system,¹⁶ the oxidation condition on the CB surface resulted in the change of the percolation time and the activation energy.

Figure 4(a,b) shows the dynamic percolation curves for PVDF/MWNT and PVDF/MWNT-COOH with various filler contents and annealed at 240°C. It was found that the dynamic percolation curves shift to a shorter percolation time at a higher MWNT concentration. The explanation is that the incorporation of more MWNTs into the polymer matrix generally results in easily constructing MWNT conductive networks because of a shorter average gap between the MWNTs.

In the previous work,¹⁹ a thermodynamic percolation model was proposed to predict the percolation time of the HDPE/iPP/VGCF system. The relationship between t_p and ϕ is given as follows:

$$t_p = -\frac{\eta}{c} \ln \frac{1 - [(1 - \phi)/\phi][\phi^*/(1 - \phi^*)]}{1 - P(0)/P(\infty)} \quad (2)$$

where η is the viscosity of the matrix at an annealing temperature, c is a constant, and ϕ is the volume fraction of filler in the matrix. ϕ^* is the volume fraction at the thermodynamic equilibrium state, and $P(0)$ and $P(\infty)$ are the fractions of the fillers which join the conduction networks at $t = 0$ and at equilibrium state ($t = \infty$), respectively. Considering the similarity of the network formation process, this thermodynamic percolation model with several modified parameters was applied to analyze the percolation time of the MWNT-filled PVDF system.

Figure 5(a,b) shows the relationship between the volume fraction of filler and $1/t_p$ for PVDF/MWNT and PVDF/MWNT-COOH annealed at various temperatures. When $1/t_p$ is extrapolated to 0, the values of ϕ^* can be obtained for MWNT- and MWNT-COOH -filled PVDF systems and are listed in Tables I and II, respectively. It was found that the ϕ^* of the PVDF/MWNT was lower than that of the PVDF/

TABLE I
Parameters of the Percolation Model
for PVDF/MWNT System

Temperature (°C)	ϕ^*	c/η	$\ln[1-P(0)/P(\infty)]$
230	0.0022	4×10^{-5}	-0.2045
240	0.0022	6×10^{-5}	-0.2057
250	0.0022	1×10^{-4}	-0.1988
260	0.0022	2×10^{-4}	-0.2047

TABLE II
Parameters of the Percolation Model
for PVDF/MWNT-COOH System

Temperature (°C)	ϕ^*	c/η	$\ln[1-P(0)/P(\infty)]$
220	0.00484	1×10^{-4}	-0.2657
230	0.00484	2×10^{-4}	-0.2832
240	0.00484	3×10^{-4}	-0.2647
250	0.00484	6×10^{-4}	-0.2801

MWNT-COOH, suggesting that the network formation of MWNTs was easier than that of MWNT-COOH. Moreover, the parameters $P(0)/P(\infty)$ and c/η are estimated from eq. (3).¹⁹

$$\ln \left[1 - \frac{P(t_p)}{P(\infty)} \right] = -\frac{c}{\eta} t_p + \ln \left[1 - \frac{P(0)}{P(\infty)} \right] \quad (3)$$

where $P(t_p)$ is the fraction of the filler in the matrix which join the conductive networks at $t = t_p$. And $P(t_p)/P(\infty)$ is given as follows:

$$\frac{P(t_p)}{P(\infty)} = \frac{\phi^*}{1 - \phi^*} \frac{1 - \phi}{\phi} \quad (4)$$

Figure 5(c,d) shows the plots of $\ln[1-P(t_p)/P(\infty)]$ versus t_p for PVDF/MWNT and PVDF/MWNT-COOH at different temperatures. A good linear relationship between $\ln[1-P(t_p)/P(\infty)]$ and t_p can be observed. The parameters $P(0)/P(\infty)$ and c/η can be calculated from the intercept and the slope of the line (see Tables I and II). The relationship between t_p and ϕ can be calculated from eq. (2), using the values listed in Tables I and II. For PVDF/MWNT and PVDF/MWNT-COOH, the relationship between ϕ and $1/t_p$ are shown as solid curves in Figure 5(a,b), respectively. It was found that the eq. (2) fits the experimental results very well, indicating that the thermodynamic percolation model can be applied for the PVDF/MWNT system.

CONCLUSIONS

PVDF-based conductive composites are prepared using pristine MWNTs and MWNT-COOH as fillers, respectively. The electrical property of the composites was investigated. It is found that the percolation threshold for PVDF/MWNT-COOH is higher than that of PVDF/MWNT, indicating that the surface characteristic of MWNTs plays an important role in the electrical properties of the composites.

In particular, we examine the dynamic process of conductive network formation in the above systems by real-time tracing the time dependency of electrical resistivity during the isothermal treatment. The percolation time for PVDF/MWNT and PVDF/MWNT-COOH composites decreases with the increase of the annealing temperature or the filler concentration. The

strong interaction between MWNNT-COOH and PVDF chains causes a reduction in mobility of the fillers, in turn an increase in the percolation time and the activation energy of the conductive network formation. These results suggest that the dynamic percolation could be used to trace the formation of filler conductive network construction and estimate the interaction between CNTs and polymer molecules. A modified thermodynamic percolation model is proposed to predict the percolation time of MWNT-filled PVDF composites, and the calculated results fit the experimental data well.

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