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Temperature and time dependence of conductive network formation: Dynamic percolation and percolation time

Cheng Zhang [a,*], Ping Wang [b], Chun-an Ma [a], Guozhang Wu [c], Masao Sumita [c]

[a] *State Key Laboratory Breeding Base for Green Chemistry Synthesis Technology, College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China*
[b] *College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China*
[c] *Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-2-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

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Abstract

Temperature and time dependence of conductive network formation in vapor-grown carbon fiber (VGCF) filled high-density polyethylene (HDPE)/poly(methyl methacrylate) (PMMA), VGCF and ketjenblack (KB) filled HDPE/isotactic polypropylene (iPP) blends have been investigated. It is found that the filled conductive polymer composites are thermodynamically non-equilibrium systems, in which the conductive network formation is temperature and time dependent, a concept named as dynamic percolation is proposed. When the composites are annealed at a temperature above the melt point of polymer matrix, the dynamic process of conductive network formation can be monitored in a real time way. Such an in situ characterization method provides more interesting information about the dispersion of conductive particles in the polymer matrix. Furthermore, a thermodynamic percolation model is modified to predict the percolation time for VGCF and KB filled HDPE/iPP multi-phase systems during the annealing treatment, and it expresses experimental results well.

Keywords: Conductive network; Electrical resistivity; Percolation

1. Introduction

The dispersion state of conductive particles in a host polymer affects the final electrical properties [1–13]. To understand the conductive network formation, percolation theory has been used to describe the relationship between the electrical conductivity and the filler content [14,15]. As the filler content increases, the composite exhibits a drastic transition from an electrical insulator to a conductor due to the formation of conductive network. The critical filler volume fraction is called percolation threshold. However, as reviewed by Lux [16], attempts to use various percolation models for the description of the filled conductive polymer composites have revealed that no existing model is able to explain all the different results of experimental studies. The disagreement may be due to the fact that the conductivity depends significantly on the geometric parameters of the filler particles, the quality of their contacts, and the interaction between the matrix and the filler [17–20].

In fact, the formation of conductive network in a conductive composite is affected not only by the filler volume fraction, but also by the preparation conditions [21–25]. Most theoretical models examining the percolation phenomenon require that conductive particles are distributed statistically and remained in their places after dispersion. If the system is at a thermodynamic equilibrium state, these prerequisites may be met. However, 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 or aggregates will inexorably tend to flocculate during aging or further processing to form a filler network. Our previous studies showed that if the as-mixed composite was molded at a temperature above the melting point of polymer matrix, an insulator-to-conductor transition was observed at a characteristic molding time even the filler content is fixed [22–28]. This percolation phenomenon suggests that conductive particles filled polymer composites have to be regarded as thermodynamic non-equilibrium systems, in which the formation of conductive networks is temperature and time dependent [29].

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* Corresponding author. Tel.: +86 571 88320253; fax: +86 571 88320253.
E-mail address: czhang@zjut.edu.cn (C. Zhang).

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In the present work, we try to investigate the temperature and time dependence of the conductive network formation in VGCF and KB filled HDPE/PMMA or HDPE/iPP blends systematically. Our previous studies showed for all the systems, carbon particles were selectively located in the HDPE phase [26–31]. In this case, two basic requirements must be fulfilled to form the conductive network throughout the composite: one is a three-dimensional filler network in the filler-rich phase, another is the continuity of this phase in the polymer blends, which were defined as double percolation. The first percolation corresponds to the conductive particles dispersion in filler-rich phase, whereas the second percolation is related to the phase morphology of the composites. Due to the selective location of conductive filler in one of the two polymer phases, a conductive composite with a low percolation threshold can be obtained successfully. It was also found that either the dispersion state of the filler or the phase morphology of the blends was influenced by the processing route.

Based on the facts that the filled conductive polymer composite is a thermodynamically non-equilibrium system, in which conductive network formation is temperature and time dependent, a concept named as dynamic percolation has been proposed [29]. In the present work, a real-time measurement method is further carried out to trace the dynamic process of conductive network formation during the annealing treatment. Such an in situ characterization method provides us more interesting information about the dispersion of conductive particles in the polymer matrix. Furthermore, a thermodynamic percolation model is modified to predict the percolation time, at which the first three-dimension filler network is constructed throughout the composites.

2. Experiment

2.1. Composite sample preparation

High-density polyethylene (HDPE) (E891(C), from Nihon Sekiyu Kagaku Co.), isotactic polypropylene (iPP) (FA110, from Showa Denko Co.) and poly(methyl methacrylate) (PMMA) (HA, from Mitsubishi Rayon Co.) are used as matrices. Vapor-grown carbon fiber (VGCF) (average length 10 μm, average diameter 0.2 μm, from Showa Denko Co.) and ketjenblack (KB) (EC, diameter 30 nm, N_2 surface area 800 m^2/g) are used as electrical conductive particles. The polymers are first mixed on a two-roll mill at 190 °C for 5 min, followed by adding the filler into the mixture and mixed for 10 min. Prior to the mixing, the polymers are dried at 80 °C for 24 h, and the filler is dried at 130 °C for 3 h under vacuum. The mixture is molten at a fixed temperature above the melting point of HDPE and hot-pressed under the pressure of 18 MPa for a given time, followed by quenching into cold water to obtain the films with the thickness of 0.5 mm. The samples for the real-time electrical measurement are pressed at 190 °C for 3 min.

2.2. Electrical resistivity measurements

Two kinds of characterization methods are carried out to investigate conductive network formation in carbon particles filled polymer composites. One is the room temperature resistivity measurement of a series of composites after they were hot-pressed at different temperatures for a varied period of time. Prior to the measurement, all the samples are kept in a vacuum at 40 °C for 24 h, and silver paste is used to ensure good contact of the sample surface with the electrodes. The electrical resistivity is measured in the thickness direction of the composite films at room temperature with a KEITHLEY 487 PICOAMMETER/VOLTAGE SOURCE. One data point is an average of three experiments.

Another method is to measure the resistivity when the samples are annealed at a given temperature above the melting point of HDPE. In this case, the specimens with the width of 14 mm and the length of 14 mm are cut from the center area of the pressed sheet and fixed between two glass slides using polyimide tapes. Silver paste is used to ensure good contact of the sample surface with the copper electrodes. The sample is placed in a temperature-controlled chamber. Nitrogen gas is introduced during the measurements in order to prevent oxidation. The applied voltage for the measurements is 1 V. The variation of the electrical resistivity over the annealing time is recorded by a computer.

2.3. Scanning electron microscopy (SEM) observation

The sheets cut from the prepared films are heated at a rate of 10 °C/min up to 200 °C, kept for 5 min, cooled at 5 °C/min–160 °C, then cooled at 0.5 °C/min–80 °C using a hot stage under nitrogen gas, finally quenched into water. The sheets throughout above treatment were used for SEM observation. The surface of the samples, which was fractured in liquid nitrogen, etched with an Eiko IB-3 and coated with Pt-Pd, is observed by an FE S800 scanning electron microscopy.

3. Results and discussion

3.1. Phase morphology, dynamic percolation and percolation time

Fig. 1 shows the SEM micrographs of KB and VGCF filled HDPE/PMMA and HDPE/iPP blends, respectively. It is clear that both HDPE/PMMA and HDPE/iPP systems present poor misbility and a two-phase structure. It can also be found that KB and VGCF are selectively located in the HDPE phase for both the systems. The mechanism of the heterogeneous distribution of fillers is explained by the difference in the affinity of fillers to each component of the polymer blends. In this case, the electrical properties strongly depend on the double percolation, i.e. the percolation of carbon particles in the filler-rich phase, and the continuity of this phase in the blends [30,31].

Fig. 2 shows time dependence of room temperature electrical resistivity for 2.5 phr VGCF filled HDPE/PMMA

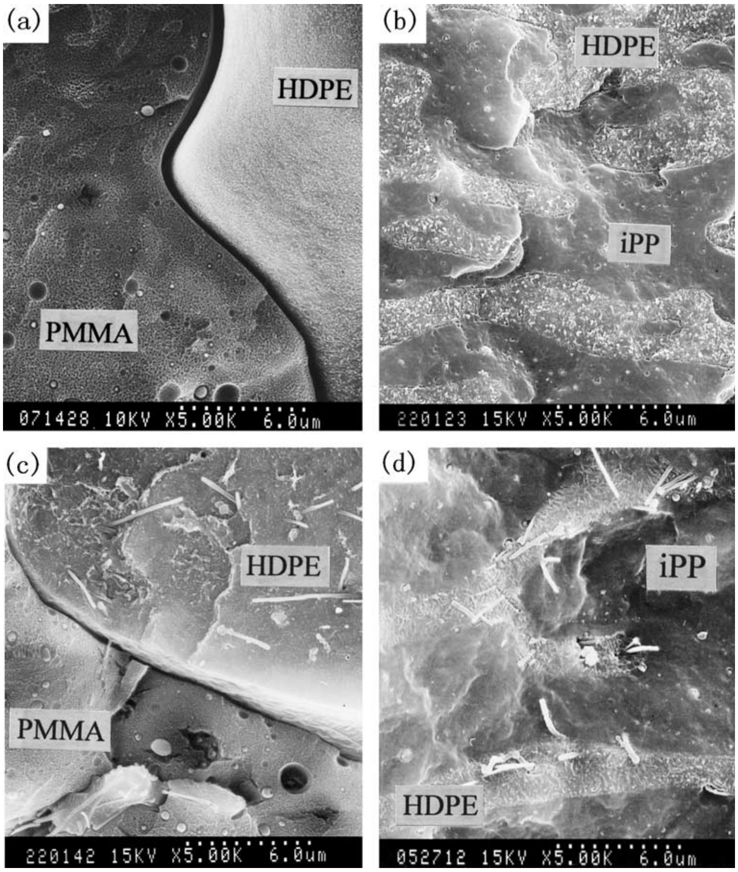

Fig. 1. SEM micrographs for 2 phr KB filled (a) HDPE/ PMMA (50/50), (b) HDPE/iPP (50/50) and 1.5 phr VGCF filled (c) HDPE/PMMA (50/50), (d) HDPE/iPP (50/50) blends.

(50/50) blend after hot-pressed at various temperatures. It can be observed that at a given temperature, the electrical resistivity decreases slightly with increasing pressing time at the early stage, and then decreases rapidly at a critical time, indicating the formation of a conductive network in the composite. This phenomenon undoubtedly originates from the aggregation and rearrangement of short carbon fibers in the filler-rich HDPE phase during the melt pressing process, indicating that percolation should be considered in terms of kinetics.

Generally, the percolation theory is often used for describing the sharp change in the electrical resistivity against the filler content for conductive particles filled polymer composites. However, the filler content is fixed in our case. In order to differentiate the relationship between the electrical resistivity and pressing time from the filler concentration dependence of percolation, we call the time dependence of percolation process as ‘dynamic percolation’. Consequently, the critical time, at which the first conductive network is constructed throughout the composite, is named as ‘percolation time’, t_p. As can be seen in Fig. 2, t_p decreases with increasing the pressing temperature. This can be attributed to the lower viscosity of the matrix at a higher temperature.

Fig. 3 presents time dependence of room temperature electrical resistivity for VGCF filled HDPE/PMMA (50/50) blends with various VGCF concentrations after hot-pressed at 190 °C. As shown, t_p shifts to a shorter pressing time at a higher VGCF loading. This is reasonable because a higher VGCF loading corresponds to a smaller average gap among carbon fibers, and thus requires a shorter pressing time for carbon fibers to coagulate with each other and to form a conductive network.

It should be pointed out that since the above resistivity measurements are done at the room temperature after the

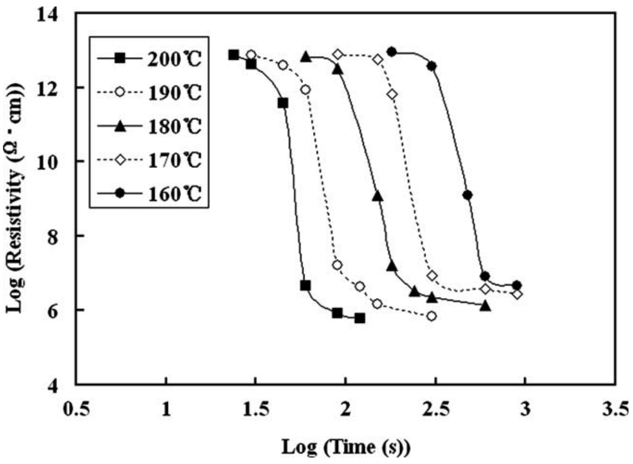

Fig. 2. Time Dependence of room temperature electrical resistivity for 2.5 phr VGCF filled HDPE/PMMA (50/50) blend after hot-pressed at various temperatures.

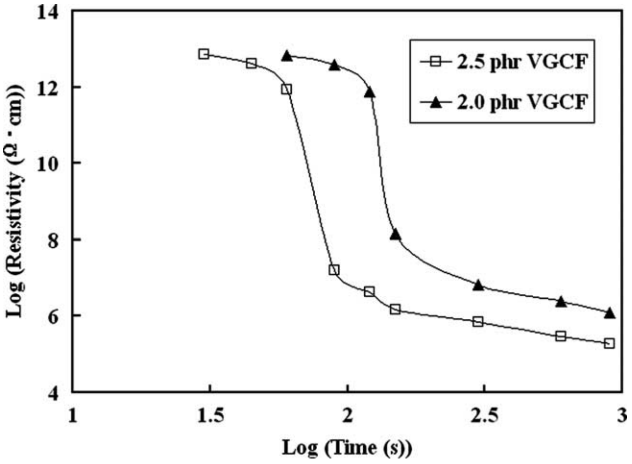

Fig. 3. Time dependence of room temperature electrical resistivity for VGCF filled HDPE/PMMA (50/50) blends with various VGCF concentrations after hot-pressed at 190 °C.

samples were hot-pressed for varied periods of time. Using this method to study the temperature and time dependence of conductive network formation is rather complex and has a lot of disadvantages. Firstly, a large number of samples are needed in order to obtain a percolation curve. It is difficult to control preparation conditions. Secondly, due to the large change in the volume of the composite from melt to solid state, the quenching process may break the conductive network, which has been formed during the pressing, and thus affect the results. Thirdly, it is fail to real-time trace the dynamic process of conductive network formation and it is difficult to determine the exact percolation time from the percolation curve. A new approach should be developed to solve the above problems.

3.2. Real-time monitoring of conductive network formation

One can expect that when the composite is annealed at a temperature above the melting point of the polymer matrix, carbon particles will move to coagulate together through the Brownian motion, and finally construct a continuous network if the amount of particles is enough. As a result, the electrical resistivity will decrease over time, and an insulator-to-conductor transition would occur at a characteristic time, indicating a dispersion/flocculation phase transition. Fig. 4 shows the variation in electrical resistivity over time (called as a dynamic percolation curve) for 0.75 phr VGCF filled HDPE/iPP (50/50) blend annealed at various temperatures. It is worth pointing out that all the specimens for the measurements are cut from one as-pressed composite sheet, so the difference among all the curves only depends on the annealing condition. As can be seen, all the curves have similar features in their shapes. At the early stage, the electrical resistivity decreases slightly over time. As the annealing time increases, a sharp decrease in the resistivity is observed at a characteristic time t_p, corresponding to the formation of the first conductive network. From the viewpoint of colloids, such a transition can be explained by the flocculation due to rearrangement and agglomeration of carbon fibers in the polymer melt. After t_p, the resistivity decreases continuously over time, indicating a further development of conductive networks in the composite. Therefore, based on dynamic percolation concept, the process of conductive network formation can be real-time traced.

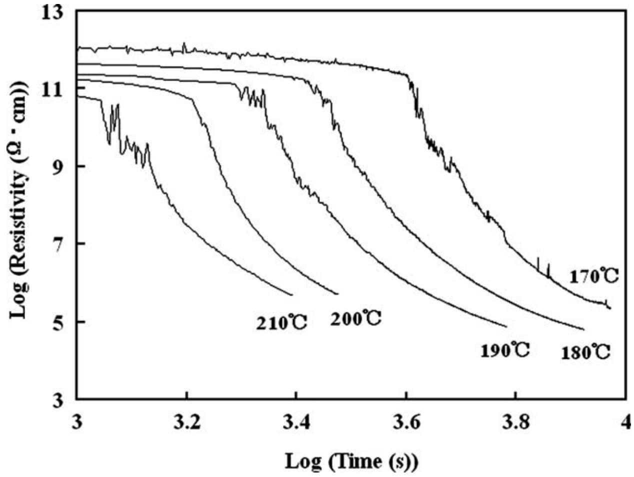

Fig. 4. Time dependence of electrical resistivity for 0.75 phr VGCF filled HDPE/iPP (50/50) blends annealed at various temperatures.

According to the studies of Sumita [17–20,32] and Wessling [33–38], the dispersion process of filler particles in the polymer matrix never lead to a thermodynamic equilibrium. Both of them emphasized the importance of the interfacial interaction at the boundary between the individual filler particles and the polymer host for the conductive network formation, and interpreted the percolation phenomenon as a phase separation process. Besides the attractive potential between the filler particles (aggregates), the flocculation process is also determined by the diffusion of the aggregates due to the Brownian motion to form thermodynamically stable agglomerates. According to Einstein–Stokes Law [39], for a given colloid system, the flocculation rate of conductive particles would be controlled by the viscosity of polymer matrix and the size of the filler particles (or aggregates). The higher the value of melt viscosity or the bigger the size of filler particle, the longer time it will take to achieve the coagulation. So, it is not surprising that the percolation time t_p decreases with increasing annealing temperature due to the low values of melt viscosity at high temperatures.

An interesting point is that all the dynamic percolation curves have similar features in their shapes. So a master curve can be obtained by shifting these curves along the horizontal axis. The similar phenomenon was observed by Wu G. et al. [40] in studying CB filled PVDF/PMMA blends. The ability to compose a single curve suggests that the primary characteristic of the conductive network structure does not change at different annealing temperatures, and the effect of annealing time can be converted with that of annealing temperature at a given VGCF content. If the shift factor α_t is defined as:

$$\alpha_t = \frac{t_p(T)}{t_p(170)} \tag{1}$$

where $t_p(T)$ is the percolation time at a annealing temperature of T, and $t_p(170)$ is the percolation time at 170 °C, by plotting

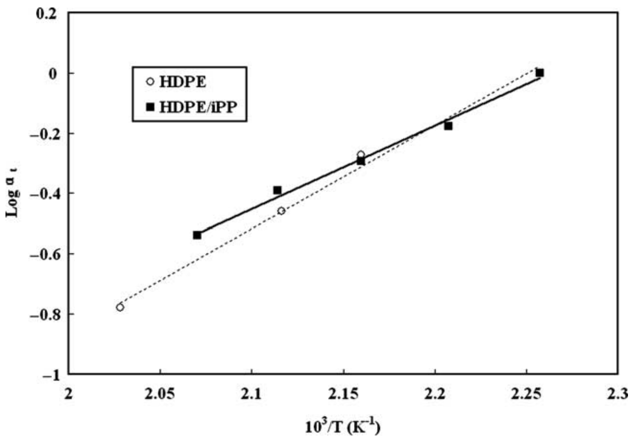

Fig. 5. Arrhenius plots of shift factor for 2.5 phr VGCF filled HDPE and 0.75 phr VGCF filled HDPE/iPP (50/50) blend.

the logarithmic shift factor against the reciprocal temperature, a good linear relationship can be observed in Fig. 5. From the slope of the plot, the activation energy is evaluated to 63.2 kJ/mol. Further study shows that the value of activation energy is not dependent on the filler concentration although t_p varies [41]. This value is slightly lower than that of 2.5 phr VGCF filled pure HDPE composite (76.4 kJ/mol) [42]. This may be one of the evidences that the formation of conductive network in the polymer blends is easier than that in pure HDPE due to the selective location of VGCF in the one of two phases.

Next, we try to clarify the influence of the filler type and content on the percolation time. Fig. 6(a) and (b) show dynamic percolation curves for VGCF and KB filled HDPE/iPP (50/50) blends with various filler concentrations annealed at 190 °C, respectively. It is clear that at a given annealing temperature, t_p decreases with increasing filler content for both the systems. It is also found that at a given filler content and annealing temperature, the values of t_p for VGCF filled system are larger than those for KB filled system. As discussed earlier, another factor influencing the kinetic process of flocculation is the average gap between filler particles (or aggregates). The average gap between filler particles (or aggregates) can be estimated by an equation proposed by Wang et al. [43]. It has been concluded that either higher filler loading or bigger specific surface area leads to a shorter interaggregate distance, thus an easier conductive network formation. At the equal filler content, since VGCF has a bigger particle size and a lower specific surface area compared to KB, a longer interaggregate distance for VGCF filled system can be expected.

Based on the above discussion, it is clear that KB and VGCF filled polymer composite systems exhibit several characteristics. First, both of them are thermodynamic unstable (non-equilibrium) systems, and show a dynamic percolation phenomenon. Secondly, the apparent percolation threshold shifts to lower filler content when the annealing temperature and time increase. Thirdly, dynamic percolation curves provide us a possibility to real-time monitor the change in the conductive particles dispersion and an in situ characterization method of conductive networks formation in the conductive polymer composites.

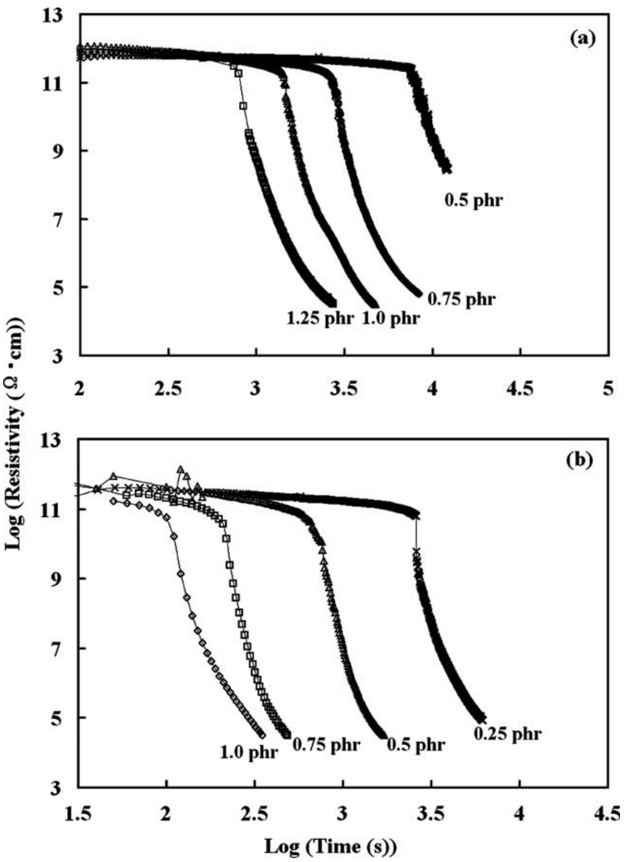

Fig. 6. Time dependence of electrical resistivity for (a) VGCF and (b) KB filled HDPE/iPP (50/50) blends with various filler concentrations annealed at 190 °C.

3.3. A model for the prediction of percolation time

Considering the dynamic percolation of the filled conductive polymer composites, the percolation time can be used as a measure to characterize the difficulty of conductive network formation. In the present section, a thermodynamic model is modified to predict the percolation time t_p for carbon particles, such as VGCF and KB filled HDPE/iPP multi-phase polymer blends systems during the annealing treatment.

It has been reported that, for a given conductive filler, the real percolation threshold, ϕ^*, increases with increasing the surface tension of polymer matrix [20]. In order to explain the dependence of ϕ^* on the polymer species, an equation has been derived by Miyasaka et al. [17] using a simple model. The most important assumption in this model is that when the total interfacial energy, Δg, resulting from carbon particles incorporated into the polymer matrix, reaches a ‘universal value’, Δg^*, carbon particles begin to coagulate each other to avoid any further increase in the total interfacial energy, and form filler networks, which facilitate electrical conduction (Fig. 7(a)). For spherical conductive particles, the final form of the equation is given as follow [17]:

$$\varphi^* = \left\{1 + \frac{3K}{(\Delta g^* R)}\right\}^{-1} \quad (2)$$

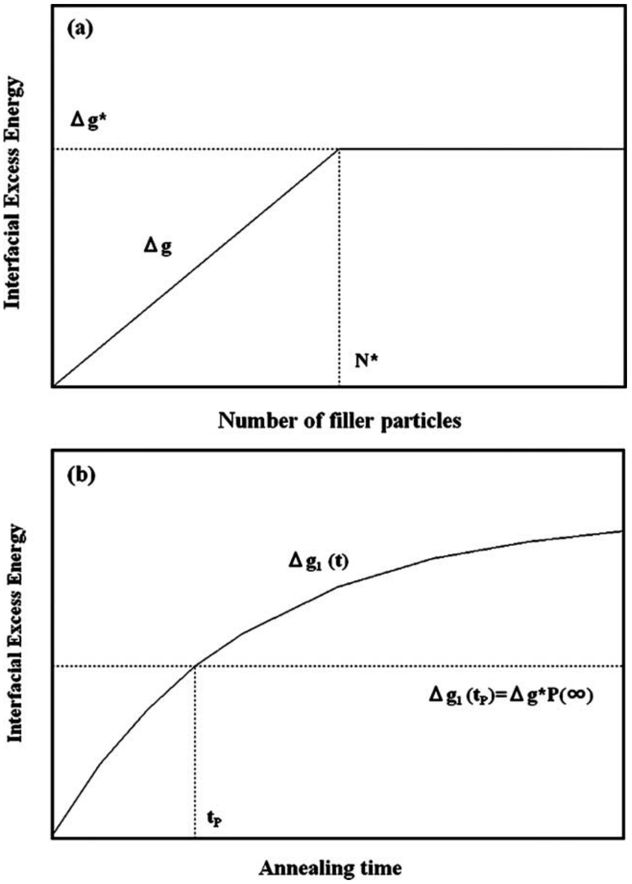

Fig. 7. Schematic representation of (a) Miyasaka's model and (b) modified model.

where K is the interfacial energy per unit area of the interface between the filler and the matrix, and R is the radius of the filler particle. According to Eq. (2), ϕ^* is determined only by the polymer species when the same filler particles are used.

It should be pointed out that the situation in our case is different from Miyasaka's one. Based on its assumptions, Miyasaka's equation is valid only in an equilibrium system. However, as discussed above, the dispersion process of filler particles in the polymer matrix never leads to a thermodynamic equilibrium. Therefore, the experimental values of percolation threshold are always larger than that of ϕ^* for a certain system. In another word, even though the volume fraction of filler particles is above ϕ^*, the as-prepared composite sample may be not conducting. Of course, if this sample is further isothermal treated for a sufficient time, conductive particles will move to coagulate together to reduce the total interfacial energy, and finally construct a continuous network. So, to predict the value of t_p, Miyasaka's model should be modified.

Since polymer blends instead of pure polymers are used as matrices in the concerned systems, several assumptions are given as follows for the simplification: (1) all the carbon particles are selectively located only in the filler-rich HDPE phase (as shown in Fig. 1); (2) carbon particles do not immigrate to the interface between two polymer phases during the annealing treatment; (3) the change in phase morphology has little influence on the conductive network formation. Then, we suppose that there are two types of carbon particles in the matrix, i.e. the carbon particles which contact each other and will join the conduction networks, CP_1, and those isolate from each other and thus will not join the networks, CP_2. Accordingly, it is considered that the fraction of the former type particles increases and that of the later ones decreases over time when the composite is annealed at a certain temperature. The volume fraction of total carbon particles in filler-rich HDPE phase is defined by

$$\phi = \frac{NV_0}{1+NV_0} \tag{3}$$

$$N = \frac{1}{V_0}\frac{\phi}{1-\phi} \tag{4}$$

where V_0 is the volume of one filler particle. N and ϕ are the number and the volume fraction of total filler particles per unit volume of HDPE matrix, respectively. Obviously,

$$N = N_1(t) + N_2(t) \quad \text{and} \quad \phi \ge \phi^* \tag{5}$$

where $N_1(t)$, $N_2(t)$ are the number of CP_1, CP_2 per unit volume of HDPE, respectively. The interface area between the polymer and isolated carbon particles (CP_2) is equal to the surface area of carbon particle (S_0). However, the interface area between the matrix and aggregated carbon particles (CP_1) is smaller than S_0 due to the aggregation. This area can be assumed to be fS_0f takes a value from 0 to1. The total interfacial energy, Δg is given by:

$$\Delta g(t) = KN_1(t)S_0f + KN_2(t)S_0 \tag{6}$$

where K is the interfacial energy per unit area of the interface between the filler particle and the matrix. In Miyasaka's case, the increase in the total interfacial energy is due to the incorporation of conductive particles into polymer matrix. Whereas in our case, the dispersion state of conductive particles in the polymer matrix already existed after the mixing. During annealing, the total interfacial energy of the system will decreases due to the agglomeration of carbon particles (Fig. 7(b)).

At annealing time t, the fraction of CP_1, $P(t) \equiv N_1(t)/N$, and the time dependence of $P(t)$ is assumed as follows [23,41]:

$$P(\infty) - P(t) = [P(\infty) - P(0)]\exp\left(\frac{-ct}{\eta}\right) \tag{7}$$

where η is the viscosity of the matrix at an annealing temperature, t is the annealing time, c is a constant, $P(0)$ and $P(\infty)$ are fractions of CP_1 at $t=0$ and at equilibrium state ($t=\infty$), respectively. $P(\infty) \le 1$ means that there is still a part of conductive particles which do not join the filler network even though the annealing time extends to infinite. Now, let us define $\Delta g_1(t) = KN_1(t)S_0$, a sum of the interfacial energy between individual particle and the matrix for CP_1. Therefore, the value of $\Delta g_1(t)$ may be larger than that of $\Delta g(t)$. Then, with Eqs. (4) and (7) we obtain

$$\begin{aligned}\Delta g_1(t) &= KNP(t)S_0\\ &= \frac{S_0K}{V_0}\frac{\phi}{1-\phi}\left\{P(\infty)-[P(\infty)-P(0)]\exp\left(\frac{-ct}{\eta}\right)\right\} \quad (8)\end{aligned}$$

when carbon particles move to form the conduction paths during annealing, $\Delta g_1(t)$, increases due to the increase of the number of CP_1. To some extent, this situation would be similar to Miyasaka's, if one considers only the increase of CP_1 number resulting from the aggregation of CP_2 in the system. It is assumed that the percolation occurs when $\Delta g_1(t)/P(\infty)$ reaches Δg^* (Fig. 7(b)), then at the percolation point:

$$\begin{aligned}\Delta g^* &= \frac{\Delta g_1(t_p)}{P(\infty)} = \frac{S_0K}{V_0}\frac{\phi}{1-\phi}\frac{P(t_p)}{P(\infty)}\\ &= \frac{S_0K}{V_0}\frac{\phi}{1-\phi}\left\{1-\left[1-\frac{P(0)}{P(\infty)}\right]\exp\left(\frac{-ct_p}{\eta}\right)\right\} \quad (9)\end{aligned}$$

Therefore, t_p can be calculated:

$$t_p = -\frac{\eta}{c}\ln\left\{\frac{1-\left[(1-\phi)/\phi\right](V_0\Delta g^*/S_0K)}{1-P(0)/P(\infty)}\right\} \quad (10)$$

where $K=\gamma_{12}$, is the interfacial energy per unit area of the interface between the filler and the matrix. In order to calculate γ_{ij}, the following equation is used [44]:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d\gamma_2^d} - 2\sqrt{\gamma_1^p\gamma_2^p} \quad (11)$$

where γ^d is the dispersion component and γ^p is the polar component of surface free energy γ, which can be referred from handbooks. The values of γ at different temperatures can be obtained from the relation: $-d\gamma/dT=0.06$, which is a general value for polymers. By using γ, γ^d and γ^p, the interfacial free energies (γ_{12}) of different systems can be calculated.

According to Eq. (10), when temperature is fixed, the percolation time t_p depends on the viscosity of matrix melt, the size of filler particle, the volume fraction of the filler and the interfacial energy of the filler/polymer interface. In order to calculate the values of t_p, first of all, the value of Δg^* should be known. Considering if $t_p=\infty$, $\phi=\phi^*$, then Eq. (9) yields

$$\Delta g* = \frac{S_0K}{V_0}\frac{\phi^*}{1-\phi^*} \quad (12)$$

thus Eq. (10) becomes:

$$t_p = -\frac{\eta}{c}\ln\frac{1-\left[(1-\phi)/\phi\right]\left[\phi^*/(1-\phi^*)\right]}{1-P(0)/P(\infty)} \quad (13)$$

The experimental points shown in Fig. 8(a) and (b) present the relationship between the volume fraction of filler in the HDPE phase and $1/t_p$ for VGCF and KB filled HDPE/iPP (50/50) composites annealed at 190 °C, respectively. If one extrapolates $1/t_p$ to 0, the values of ϕ^* can be obtained for the two systems and listed in Table 1. Using Eq. (12), the value of Δg^* can be evaluated. To estimate the parameters $P(0)/P(\infty)$ and c/η, one can use the following equation (Eq. (7)):

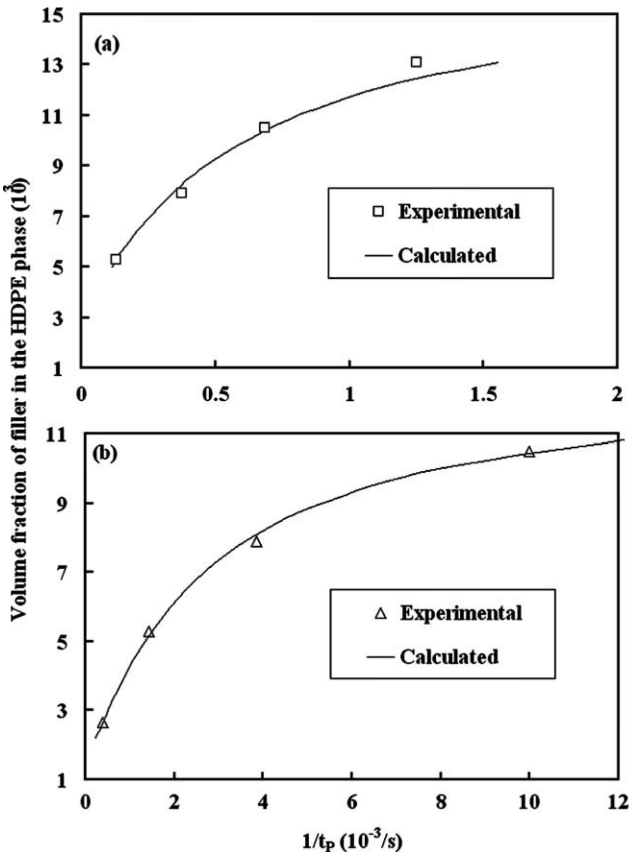

Fig. 8. Plots of filler volume fraction in the HDPE phase versus $1/t_P$ for (a) VGCF and (b) KB filled HDPE/iPP (50/50) blends annealed at 190 °C.

$$\ln\left[1-\frac{P(t_p)}{P(\infty)}\right] = -\frac{c}{\eta}t_p + \ln\left[1-\frac{P(0)}{P(\infty)}\right] \quad (14)$$

where (Eqs. (4), (9) and (12))

$$\frac{P(t_p)}{P(\infty)} = \frac{V_0}{S_0K}\frac{1-\phi}{\phi}\Delta g^* = \frac{\phi^*}{1-\phi^*}\frac{1-\phi}{\phi} \quad (15)$$

Fig. 9(a) and (b) show the plots of $\ln[1-P(t_p)/P(\infty)]$ versus t_p for VGCF and KB filled HDPE/iPP (50/50) systems annealed at 190 °C, respectively. 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 obtained from the intercept and the slope of the line, and are listed in Table 1. Using parameters S_0, V_0, K,Δg^*, $P(0)/P(\infty)$ and c/η, the relationship between t_p and ϕ, is described as Eq. (10).

Table 1
Parameters for VGCF and KB filled HDPE/iPP (50/50) blends

Carbon particle	ϕ^*	c/η	$\ln[1-P(0)/P(\infty)]$
VGCF	0.0039	1.42×10^{-4}	−0.258
KB	0.0019	4.27×10^{-4}	−0.155

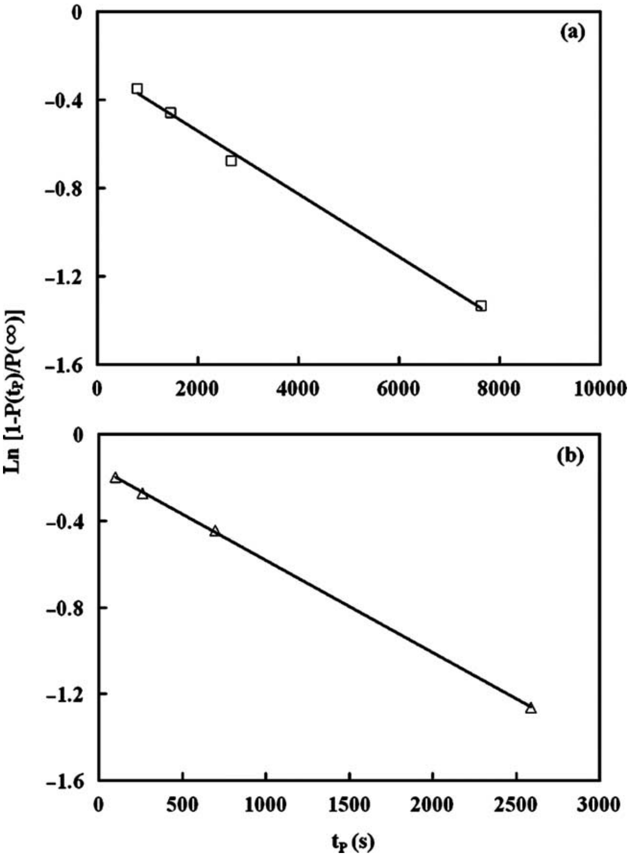

Fig. 9. Plots of $\ln[1-P(t_P)/P(\infty)]$ versus t_p for (a) VGCF and (b) KB filled HDPE/iPP (50/50) blends annealed at 190 °C.

Of course, if one does not know the characteristics of the matrix and the filler, such as S_0, V_0 and K, the relationship between t_p and ϕ, can also be directly calculated from Eq. (13) using the values of ϕ^* listed in Table 1. For VGCF and KB filled HDPE/iPP (50/50) systems, the relationships between ϕ and $1/t_p$, are shown as two solid curves in Fig. 8(a) and (b), respectively. As can be seen, Eq. (13) expresses the experimental results well.

4. Conclusions

The temperature and time dependence of conductive network formation indicates that the conductive particles filled polymer composites are thermodynamic non-equilibrium systems. The percolation time t_p decreases with increasing filler content at a given temperature, and increases with decreasing temperature at a given filler content. The dynamic process of conductive network formation can be in situ traced during the annealing treatment. Based on theoretical analysis of dynamic percolation curves, the temperature and time dependence of conductive network formation can be estimated quantitatively. Percolation time t_p can be used as a measure to characterize the difficulty of conductive network formation. A thermodynamic percolation model is modified to describe the relationship between t_p and the volume fraction of the filler. It expresses experimental results well.

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