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# Landau Mean-Field Approximation of Percolation in Conductive Polymer Composites

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**Summary:** A novel approach of the percolation behavior in conductive composites was proposed on the basis of Landau mean-field theory. The percolation transition is treated as a concentration-derived phase transition of conductive particles from dispersion to flocculation so as to form a dissipative percolating network. A formulation of conductivity as a function of filler volume fraction in the percolation transition region was established, which was validated in high-density polyethylene/carbon black (HDPE/CB) composites from two different laboratories and also in cured epoxy/CB composites of Fournier et al. At high CB concentrations above the percolation threshold, the conductive behavior in HDPE/CB composites follows the statistical percolation theory.

**Keywords:** conductive composite; landau mean-field theory; percolation

## Introduction

Conductive polymer composites are of academic and technical importance due to their wide applications in industry.[1–4] One of the well-known electric properties is the non-linear dependence of conductivity $\sigma$ on filler volume fraction $\Phi$, which is referred to as percolation of conduction.[5–8] There are two characteristic transitions in $\sigma$ as a function of $\Phi$ (Figure 1). The first occurs at $\Phi_{c1}$ across which $\sigma$ increases remarkably whereas the second appears at $\Phi_{c2}$ above which $\sigma$ levels off. In the percolation transition region from $\Phi_{c1}$ to $\Phi_{c2}$, $\sigma$ increases by several orders of magnitude.

Extensive studies have been conducted on the percolation of carbon black (CB)-filled polymer composites. Several models have been proposed to understand the percolation behavior.[9] The general effective medium (GEM) concept has proven an important theoretical advance towards understanding the structure–property relationship in a percolation system.[10] The GEM expression at $\Phi$ above the threshold can be reduced to the statistical percolation theory [11]

$$\sigma = \sigma_0(\Phi - \Phi_{c2})^t \tag{1}$$

taking conductivity of the insulating phase as zero.[12] Here, $t$ is a critical exponent, and $\sigma_0$ is a constant depending on the details of the electron transports. The major restriction of the GEM equation is in the neglecting of the real geometrical arrangement and aggregation of the particles.[13] The introduction of the percolation theory accounts for the network formation in the systems. Theoretically, $t$ is a universal constant independent of the chemical nature and geometries of the constituents.[11] $t=1.6$ has been predicted[11,14] for three-dimensional systems while computer simulations give $t=2.0$.[15] The latter has been verified in diverse composites[16–27] and has been currently accepted as the universal value. However, $t$ values significantly higher than 2.0 have been observed,[28–40] and the mean-field value $t=3.0$ has been also verified in some systems.[28,31,40–44] In fact, a vast class of disordered conducting–insulating compounds close to the percolation threshold is characterized by non-universal values of $t$ greater than 2.0.[45] The

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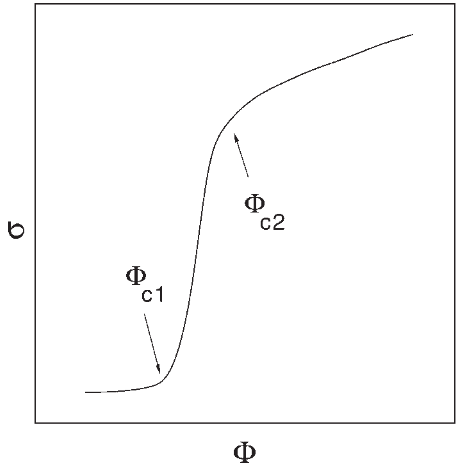

*Figure 1.*
Percolation transition for polymer conductive composites.

non-universal exponent may be considered as a proof of the inadequacy of the lattice percolation theory to account fully for conduction.

On the other hand, continuum percolation theories predict non-universal behavior of $t > 2.0$ for an anomalous diverging distribution of resistance between conductive elements[46] and for a tunneling conduction between conductive elements,[30] or $t < 2.5$ for a Swiss-cheese model where spherical voids are introduced in a continuous conductor.[47] Heaney argued that, in CB-filled polymer composites, long-range interactions could drive the system towards the mean-field regime with $t = 3.0$.[41] The values of $t$ even larger than the mean-field value in some CB-filled polymer composites[32,40] can be explained by a tunneling-percolation model[48] or a combination of point contacts and the Swiss Cheese model.[49] The non-universal percolation found in different composites suggests that the conduction might be related to the assembling morphologies of conductive fillers[50] or the microstructure of the percolating network.[21,27,30,51] However, it is different to probe the underlying origin of the non-universal percolation based on available continuum percolation theories.

It is well known that high energy input is necessary to prepare multiphase composites, and an entropy export is expected to accompany the formation of a well-ordered network from randomly dispersed particles.[52] The percolating network forms under non-equilibrium thermodynamic conditions in existence of energy exchange between the system and the surroundings. Appreciable flocculation of CB particles may occur in filled polymers during their storage even in the absence of shear.[53] Wessling proposed a model of dispersion/flocculation phase transition for the $\sigma$ jump at a critical concentration, and argued that both the energy input and the entropy output might be related to Φ while they become much greater around the critical concentration.[52,54] The interaction between particles not only influences the value of the percolation threshold[55,56] but also plays a crucial role for the dispersion/flocculation phase transition so that the conductive particles arrange themselves into thin and elongated clusters and further a flocculent phase or percolating network.

From the thermodynamic viewpoint, the formation of a percolating network should correspond to or a geometrical phase change via particle self-organization in the conductive phase. In the present article, we propose a novel approximation of the conduction in the percolation transition region ($\Phi_{c1} < \Phi < \Phi_{c2}$) on the basis of Landau mean-field theory.

## Experimental Part

### Materials

High density polyethylene (HDPE) 2480 (melting index 0.014 g/min; density 0.942 g/cm$^3$; melting point 127 °C) and 5000s (melting index 0.090 g/min; density 0.954/cm$^3$; meting point 128 °C) were used as a matrix, and carbon blacks N550 (Mean particle diameter 77 nm; BET surface area 43 m$^2$/g; Iodin absorption 43 mg/g; DBP absorption 1.21 cm$^3$/g; Volatile 1.2%) and N330 (Mean particle diameter 40 nm; BET surface area 80 m$^2$/g; Iodin absorption 82

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mg/g; DBP absorption 1.02 $cm^3/g$; Volatile 2.2%) as conductive filler.

### Preparation of Composites

The composites were prepared by the conventional compounding of the polymer and the filler at $165 \pm 5\,^\circ C$ for 10 min on a two-roll mill, followed by a compression molding at $165 \pm 5\,^\circ C$ for 10 min under 100 $kg/cm^2$ to form sheet samples ($15 \times 15 \times 2\ mm^3$). Two pieces of copper nets were mounted onto the opposite wide surfaces of the sheet to ensure good electrical contact with the attached copper electrodes.

### Resistance Measurement

Two-probe resistance measurements were carried out using a M890B$^+$ digital multimeter (Shenzhen Huayi Mastech Co., China) when resistances were lower than $10^{10}$ Ω while a high resistance meter (ZC36, Shanghai Precise Science Instrument Co., China) was used to measure resistance above $10^{10}$ Ω. Resistivity was determined by averaging the measured values from 10–30 samples.

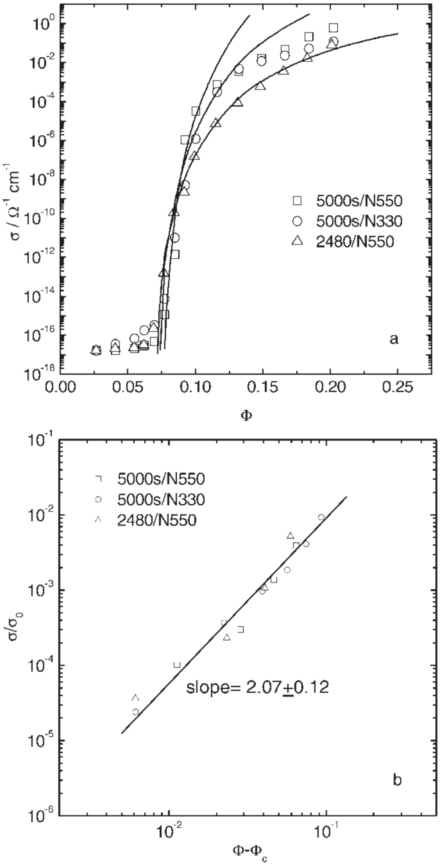

*Figure 2.*
Conductivity $\sigma$ as a function of filler volume fraction $\Phi$ for three HDPE/CB composites. The solid curves in (a) are calculated according to Equation (5b). Part (b) shows the plot according to the theoretic formulation of the statistical percolation.

## Results and Discussion

Figure 2(a) shows the $\sigma$ to $\Phi$ relationships for three HDPE conductive composites prepared. $\sigma$ jumps more than 13 orders of magnitude over the percolation region from $\Phi_{c1}$ to $\Phi_{c2}$. Using $\Phi_{c2}$ as an adjustable parameter, we plot $\sigma/\sigma_0$ as a function of $(\Phi - \Phi_{c2})$ in Figure 2(b). The data are collapsed onto a straight line which could be formulated by Equation (1), proving that the conduction above $\Phi_{c2}$ follows the same mechanism. Table 1 lists the values of $\Phi_{c2}$ and $\sigma_0$.

The particles are homogeneously dispersed in the matrix at $\Phi < \Phi_{c1}$ while they come into contact and form infinite clusters for the first time as $\Phi$ approaches $\Phi_{c1}$ from below. In the close vicinity of $\Phi_{c1}$, the conducting phase becomes more ordered with the appearance of infinite clusters and the spatial concentration fluctuation of the conductive elements is inclined to infinity so that the percolation might be considered as a geometrical phase transition.[57] A correlation length emerges and grows rapidly, resulting in the $\sigma$ singularity in the close vicinity of $\Phi_{c1}$.[58–61] The electronic transports are thus determined by all the infinite clusters, independent of the details of the microscopic or local structures of the percolating network. As a critical phenomenon, continuous phase transitions can be related to the singularity of thermodynamic potential around the critical point, i.e., the thermodynamic potential and its first-order differential change continuously while its second-order differential discontinuously at $\Phi_{c1}$.[57]

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**Table 1.**
Parameters in Equation (1) and Equation (5b) for HDPE/CB conductive composites.

| Composite | $\Phi_{c2}$ | $\sigma_0/\Omega^{-1}cm^{-1}$ | $\Phi_{c1}$ | $(a/b)^{0.5}$ |
|---|---|---|---|---|
| 5000s/N550 | 0.138 | 158 | 0.078 | 60.0 |
| 5000s/N330 | 0.110 | 12 | 0.074 | 52.0 |
| 2480/N550 | 0.142 | 15 | 0.072 | 45.0 |

An order-parameter is usually introduced to describe the order changes in a continuous phase transition.[62] At the critical point, the order-parameter in a new phase grows continuously from zero, which is a kind of macroscopic parameter, a scalar, a vector, or a tensor. While a variety of order-parameters might be defined for the percolation, we use a variable $\Sigma = \ln(\sigma/\sigma_p)$ considering $\Sigma \approx 0$ at $\Phi < \Phi_{c1}$ and $\Sigma \gg 0$ at $\Phi > \Phi_{c1}$. When using $F = 1/\Phi$ as an independent variable, the $\Sigma$ to $F$ relationship that describes the percolation seems to accord with the general characteristic of a continuous phase transition, as illuminated by an example of 5000s/N550 in Figure 3.

Landau mean-field theory is one of the simple theories that deal with continuous phase transitions losing symmetry at critical conditions. Anisimov et al. attempted to make a thermodynamic description of the phase transition of micelle formation within the framework of Landau mean-field theory.[63] Because $\Sigma$ is considerably small (theoretically, zero) at the critical point $F_c$, the Landau free energy can be assumed as a function of $F$ and $\Sigma$ as

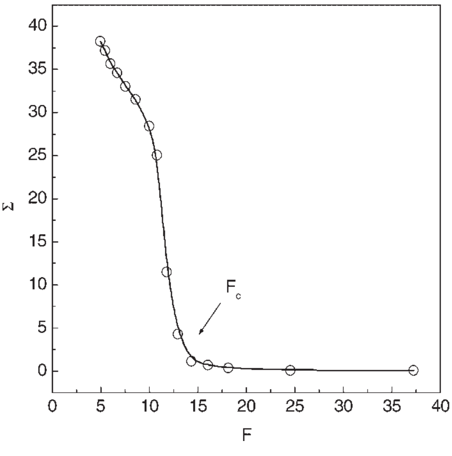

**Figure 3.**
Conduction order-parameter $\Sigma$ as a function of reciprocal of filler volume fraction $F = 1/\Phi$.

$$G(\Sigma, F) = G_0(F) + \frac{1}{2}a(F)\Sigma^2 + \frac{1}{4}b(F)\Sigma^4 + \cdots \quad (2)$$

where $G_0(F)$ is the potential at $\Sigma = 0$ and $a(F)$ and $b(F)$ are adjustable parameters. $a(F)$ should be so selected that $G(F,\Sigma)$ minimizes at $\Sigma = 0$ when $F \geq F_c$ and at $\Sigma \neq 0$ when $F < F_c$. $G(F,\Sigma)$ minimizes only if $(\partial G/\partial \Sigma)_F = 0$ and $(\partial^2 G/\partial \Sigma^2)_F > 0$, which requires $a(F) > 0$ at $F > F_c$ and $a(F) < 0$ at $F < F_c$. $a(F) = 0$ is predetermined at $F = F_c$ where $G(F,\Sigma)$ changes continuously. Accordingly, $a(F)$ can be expressed as

$$a(F) = a(F - F_c)/F_c \quad (a > 0) \quad (3)$$

where $a$ is a positive constant. Considering the thermodynamic stability, $b(F)$ must be taken as a positive constant, i.e., $b(F) = b > 0$.

From $(\partial G/\partial \Sigma)_F = 0$ and $(\partial^2 G/\partial \Sigma^2)_F > 0$, one obtains

$$\Sigma^2 = -(a/b) \cdot (F/F_c - 1) \quad (F < F_c) \quad (4a)$$

$$\Sigma^2 = 0 \quad (F > F_c) \quad (4b)$$

The $\sigma \sim \Phi$ relationship can be then expressed as

$$\sigma = \sigma_p \quad (\Phi < \Phi_c) \quad (5a)$$

$$\ln(\sigma/\sigma_p) = (a/b)^{1/2} \cdot (1 - \Phi_c/\Phi)^{1/2} \quad (\Phi > \Phi_c) \quad (5b)$$

Taking $\Phi_c = \Phi_{c1}$, the predictions from Equation (5b) are presented as solid curves in Figure 2(a) and the parameters are listed in Table 1. The prediction accords with the measured data in the 2480/N550 composite over the whole concentration range investigated. On the other hand, the predicted values become higher than the measured ones from $\Phi = 0.103$ and $\Phi = 0.133$ for the 5000s/N550 and the 5000s/N330 composites, respectively. Nevertheless, Figure 2(a) shows that Equation (5b) with only one dimensionless adjust parameter $(a/b)^{1/2}$ can well account for the conduction during the percolation transition.

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Karasek et al. found that the electrical percolation threshold is in very good agreement with the filler concentration where all CB particles form with the polymer chains a coherent three-dimensional gel structure.[64] The downward deviation of $\sigma$ at $\Phi > \Phi_{c2}$ from the prediction of Equation (5b) might be related to the cluster growth mechanism above the gel point $\Phi_{c2}$ different from that in the percolation transition region ($\Phi_{c1} < \Phi < \Phi_{c2}$).[65] In the regime of percolation transition, the restricted mobility of the dispersed aggregates governs the cluster growth and the neighboring clusters are separated by thin layers of polymer. The tunneling gaps between neighboring clusters are joined together in a bond percolating process, which determines the conduction. At $\Phi > \Phi_{c2}$, upon contact of neighboring particles or clusters, they stick together and irreversibly form larger cluster because the thermal energy of colloidal particles is in general much smaller than their interaction energy.[66]A fractal filler network forms that corresponds to a space-filling configuration of kinetic cluster–cluster aggregation (CCA) while smaller clusters occupy less empty space than larger clusters. The conduction process becomes nearly ohmic in nature and a scaling invariant power law of Equation (1) arises.[67]

We also examine the $\sigma$ to $\Phi$ relationships of three HDPE/CB composites with very different percolation thresholds. The data of Nakamura et al.[68] were extracted and are replotted in Figure 4. We fit the data at $\Phi_{c1} < \Phi < \Phi_{c2}$ applying Equation (5b), as shown by the solid curves in this figure. The calculated curves describe well the experimental data up to the highest concentration for the two composites containing Ketjenblack and Asahi-thermal. For the HDPE/#45 composite, the predicted curve becomes higher than the experimental data at $\Phi > 0.097$. Again, the conduction follows Equation (1) at $\Phi > \Phi_{c2}$.

The theoretic formulation in fact does not involve the first-order phase transition of the matrix. The existence of the crystalline phase only dilutes the concentration of the conductive phase. It implies that Equation (5b) is universal, which should be further examined in amorphous and/or

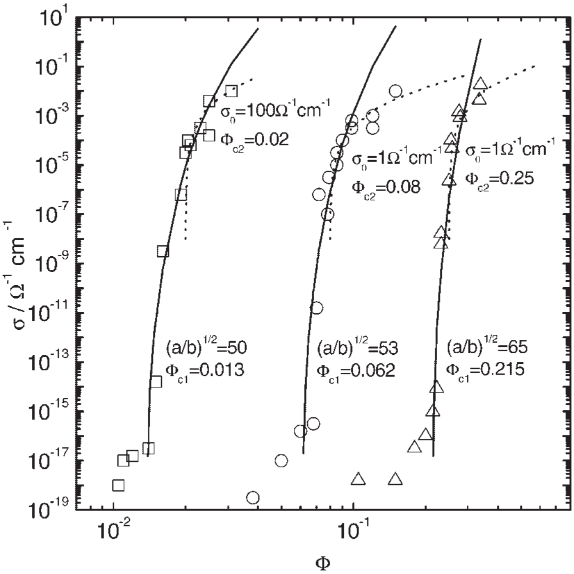

***Figure 4.***
Relationship between $\sigma$ and $\Phi$ for HDPE filled with CB of Ketjenblack (□), #45 (○) and Asahi-thermal (△). The data point was taken from Nakamura et al.[68] and the curves are calculated according to Equation (5b).

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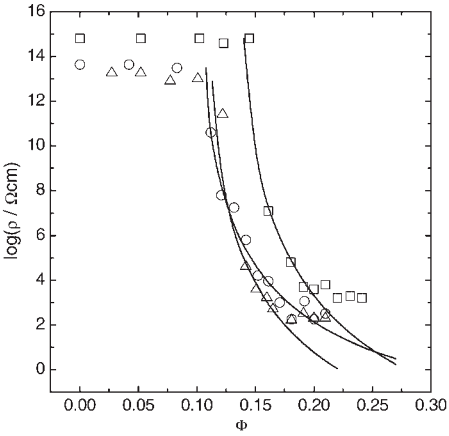

***Figure 5.***

Relationship between resistivity $\rho$ and $\Phi$ for amine cured diglycidyl ether of bisphenol A epoxy resin filled with CB. The data point was taken from Fournier et al.[69] and the curves are calculated according to Equation (5b).

thermoset composites. We here make a brief examination of resistivity $\rho$ as a function of $\Phi$ for a CB-filled epoxy resin. The data of Fournier et al.[69] was replotted in Figure 5. The macromolecular structure of the matrix changes with amine hardener, which influences $\Phi_{c1}$ significantly. However, the calculated curves agree well with the experimental data in the percolation transition region. Further work should be done to reveal the physical meaning of $(a/b)^{1/2}$ and its dependence on the physical properties of the matrix and the conductive phase. The present study gives $(a/b)^{1/2} = 54.2 \pm 7.2$ averaged from six HDPE/CB composites and $(a/b)^{1/2} = 19.0 \pm 2.0$ from three epoxy/CB composites. It seems that the $(a/b)^{1/2}$ value is independent of the CB structure but rather sensitive to the nature of the matrix or the interaction between the CB particle and the matrix.

## Conclusions

The percolation behavior in conductive composites is considered as a dispersion/flocculation phase transition controlled by the filler concentration. On the basis of the Landau mean-field theory, a formulation is suggested for describing the $\sigma$ to $\Phi$ relationships in the percolation transition region, which is validated in HDPE/CB composites from two laboratories and also in cured epoxy/CB composites by Fournier et al.[69]

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