

# Electric Conductivity of PS/PA6/Carbon Black Composites

Zhongbin Xu,<sup>1,2</sup> Chao Zhao,<sup>2</sup> Aijuan Gu,<sup>1</sup> Zhengping Fang<sup>1</sup>

<sup>1</sup>Institute of Polymer Composites, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China

<sup>2</sup>State Key Laboratory of Polymer Reaction Engineering, College of Materials Science and Chemical Engineering, Zhejiang University Hangzhou, Zhejiang 310027, People's Republic of China

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**ABSTRACT:** Polystyrene (PS)/nylon6 (PA6)/carbon black (CB) composites were prepared in Haake rheometer. The factors influencing the electric conductivity of PS/PA6/CB composites were investigated. Results showed that CB particles only distribute in PA6 phase because of the strong polarity of PA6. The CB content in PA6 phase and the morphology of PA6/CB phase affect the electric conductivity of PS/PA6/CB composites. No matter the PA6/CB phase is continuous or dispersed, the electric conductivity of PS/PA6/CB composites increases with the increase of CB content in the PA6 phase; higher continuous degree of PA6/CB phase leads to higher electric conductivity. A new term, statistical average critical distance (SACD), was defined to explain the

electric mechanism of PS/PA6/CB composites, which is a function of CB content in PA6. The SACD of PS/PA6/CB composites, in which CB content is 23 wt % in PA6, was quantitatively counted, which is about 54 nm. Keeping the CB content in composites at 5.67 wt %, the optimum mass ratio of PS/PA6 for the composites having the highest electric conductivity is 80 : 20, resulting from the competitive result of the earlier two factors (that is the CB content in PA6 phase and the morphology of PA6/CB phase). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1042–1047, 2007

**Key words:** polymer blend; morphology; carbon black; electric conductivity; statistical average critical distance

## INTRODUCTION

Carbon black (CB) have been often used as the additive of single polymer to prepare electric conductive materials, however, the content of CB is usually so high that it leads to increase the melt viscosity of the polymer and decrease the mechanical properties of the polymer.<sup>1,2</sup> One of recent trends is to use multiphase polymer blends to reduce the amount of conductive fillers in composites.<sup>3,4</sup> The selective distribution of CB into one phase of polymer blends can produce conducting material at a lower filler content. This can also provide better process ability and avoid poor mechanical properties caused by high-filler loading.

Stephen<sup>3</sup> investigated the electric conductivity of composites composed of poly(ethylene-co-vinyl acetate) (EVA), high density polyethylene (HDPE), and CB, where CB located preferentially into the HDPE phase. The blends exhibited reduced percolation thresholds and enhanced electric conductivity above that of the individually CB-filled HDPE and EVA.

Tchoudakov<sup>4</sup> studied the electric resistivity and morphology of polypropylene/nylon (PP/Ny) immiscible blends incorporated with CB. CB was found to

be preferentially located in the Ny phase or upon the Ny/PP interface. Blends with a cocontinuous phase morphology depicted especially low resistivity values due to a "double percolation" effect. The two-phase morphology in the PP/Ny immiscible blends and the preferential localization of the CB particles in the dispersed Ny phase cause the effective CB content to be significantly higher than its nominal value. Hence, conductive polymer systems can be achieved at rather lower CB loadings than required for turning a single polymer into a conductor.

Li<sup>5</sup> studied the CB distribution and the relationship between morphology and electric properties of the PP/epoxy/CB composites. In PP/epoxy/CB composites, CB particles preferentially located in the epoxy phase. The incorporation of CB changed the spherical particles of the dispersed epoxy phase into elongated structure, and with the increase of epoxy content the elongation deformation of epoxy phase became more obvious and eventually the blends developed into cocontinuous structure. When the weight ratio of PP/epoxy was 40/60, the percolation threshold of CB content reduced to about 4 phr, which is half of that in PP/CB composite.

Huang<sup>1</sup> pointed out that when binary blends are considered, the percolation threshold depends strongly on the phase morphology and the distribution of CB in the polymer blend. When CB is added into an immiscible polymer blend, it is distributed in different proportions depending upon its affinity to

Correspondence to: A. Gu (aijuangu@126.com).

**TABLE I**  
Formulations of System I

System I	Mass of PS/PA6/CB (g)
Ia (IIIe, IVf)	40/10/3
Ib	40/10/4
Ic	40/10/6

the polymer components and the processing history. There are two types of distribution that are beneficial to electric conduction. One is distributed predominantly in one continuous phase, and the other is located preferentially at the interface. When CB preferentially locates in one phase, the phase changes from a dropwise domain into a cocontinuous structure, and the mixture of the two polymers becomes conductive. Gubbels<sup>6</sup> studied the kinetic and thermodynamic control of the selective localization of CB at the interface of immiscible polymer blends to make CB particles located preferentially at the interface.

Earlier studies and other similar works obtained valuable results,<sup>7-11</sup> however, less work is done related the subject on the electric conductivity of composites in which CB particles only distribute in dispersed phase, and even less studies on the conductive mechanism of such composites. In this article, polystyrene (PS)/nylon6 (PA6)/CB system was designed to study the factors affecting the electric conductivity of PS/PA6/CB composites. The emphasis was put on investigation of the electric conductivity of composites, in which CB particles only distribute in dispersed phase and the correspondingly electric conductivity mechanism.

## EXPERIMENTAL

### Materials

PA6, 1013B ( $M_w = 20,000$ ;  $\rho = 1.13 \text{ g/cm}^3$ ) was supplied by Ube Industries (Japan). PS ( $M_w = 200,000$ ;  $\rho = 1.05 \text{ g/cm}^3$ ) and GPPS 158 K was supplied by Bassel (Germany). CB (HCB-A) was a commercial product supplied by Agrofert (Czechoslovakia).

### Preparation of PS/PA6/CB composites

Prior to blending, PA6 was dried at 100°C in vacuum for about 12 h. Unless otherwise specified, the PS/PA6/CB composites were prepared by the following procedure: first PS, PA6, and CB were blended to form a dry mixture, and then the dry mixture was put into a Haake HBI System90 Rheometer (Germany) followed by melt-mixing at 230°C for 10 min with a rotating speed of 100 rpm to form PS/PA6/CB composites.

**TABLE II**  
Formulations of System II

System II	Mass of PS/PA6/CB (g)
IIa	25/25/1
IIb	25/25/1.25
IIc	25/25/2
IId	25/25/3
IIe	25/25/4
IIg	25/25/5
IIh	25/25/6
IIi	25/25/7
IIj	25/25/8

Four systems of formulations (Tables I–IV) were designed to study the factors, which influence the electric conductivity of PS/PA6/CB composites. T3 T4

### Characterization

The distribution state of carbon black (CB) particles and the morphology of PS/PA6/CB composites were determined by using a JEM-200EX TEM (Japan) at an acceleration voltage of 120 kV.

The electric conductivity of the PS/PA6/CB composites was measured with EDM-1341 multimeter (Taiwan). To measure electric conductivity of composites, samples were prepared by the following procedure: first, the composite prepared earlier was subsequently compression-molded at 200°C for 3 min to form a round slice (thickness = 3 mm, diameter = 2 cm), then the slice was covered with a piece of copper net on each side of the slice followed by compression molding at 200°C for 3 min to obtain samples for measuring electric conductivity.

About 500 distances between PA6/CB phase particles located nearby were freely selected on the TEM pictures of a sample, and their distances were counted and averaged with ImageTool software to get the statistical average critical distance (SACD) value.

**TABLE III**  
Formulations of System III

System III	Mass of PS/PA6/CB (g)
IIIa	5/10/3
IIIb	10/10/3
IIIc	20/10/3
IIId	30/10/3
IIIe	40/10/3
IIIf	45/10/3
IIIg	50/10/3
IIIh	55/10/3
IIIi	60/10/3
IIIj	70/10/3
IIIk	80/10/3

**TABLE IV**  
**Formulations of System IV**

System IV	Mass of PS/PA6/CB (g)
IVa	10/40/3
IVb	20/30/3
IVc	30/20/3
IVd	35/15/3
IVf	40/10/3
IVg	42/8/3

## RESULTS AND DISCUSSION

### The selective distribution of CB particles in PS/PA6/CB composites

The morphological observations of PS/PA6/CB composites with different formulations are shown in Figure 1. It demonstrates clearly that (1) no matter the PA6 phase is continuous or not, CB particles preferentially locate in the PA6 phase and no CB particles locate in PS phase. The reason of this phenomenon is that the polarity of PA6 is much larger than that of PS; (2) the increase of CB content in PA6 does not change the morphology of PS/PA6/CB composites significantly, and PA6/CB phase remains dispersed phase when the CB content in PA6 increases from 23 to 38 wt % in PS/PA6/CB composites [Fig. 1(a)–(c)].

### Effect of the CB content in PA6 phase on the electric conductivity of PS/PA6/CB composites

Figure 1 clearly shows that CB particles preferentially locate in the PA6 phase and no CB particles locate in PS phase. So, it is guessed that CB content in PA6 may be a factor, which influences the electric conductivity of the composites. Because the morphology of composites are changed with the different mass ratio of PS/PA6, as shown in Figure 1, two kinds of composites (System I and System II) were designed, in which the mass ratio of PS/PA6 is 40/10 or 25/25. Accordingly, the PA6 phase is dispersed or continuous phase, respectively, were designed to study the effect of CB content in PA6 on the electric conductivity of the composites with different morphology of PA6/CB phase, and the results are depicted in Figure 2. In case of the System I, in which PA6/CB phase is dispersed phase, the electric conductive ability of these PS/PA6/CB composites is high, indicating that there exist networks for the electrons to transmit. Moreover, Figure 2 shows that the electric conductivity gets higher with the increase of the CB content in PA6 phase.

For the System II, in which PA6/CB phase is continuous phase, the electric conductivity of PS/PA6/CB composites increases almost linearly with the

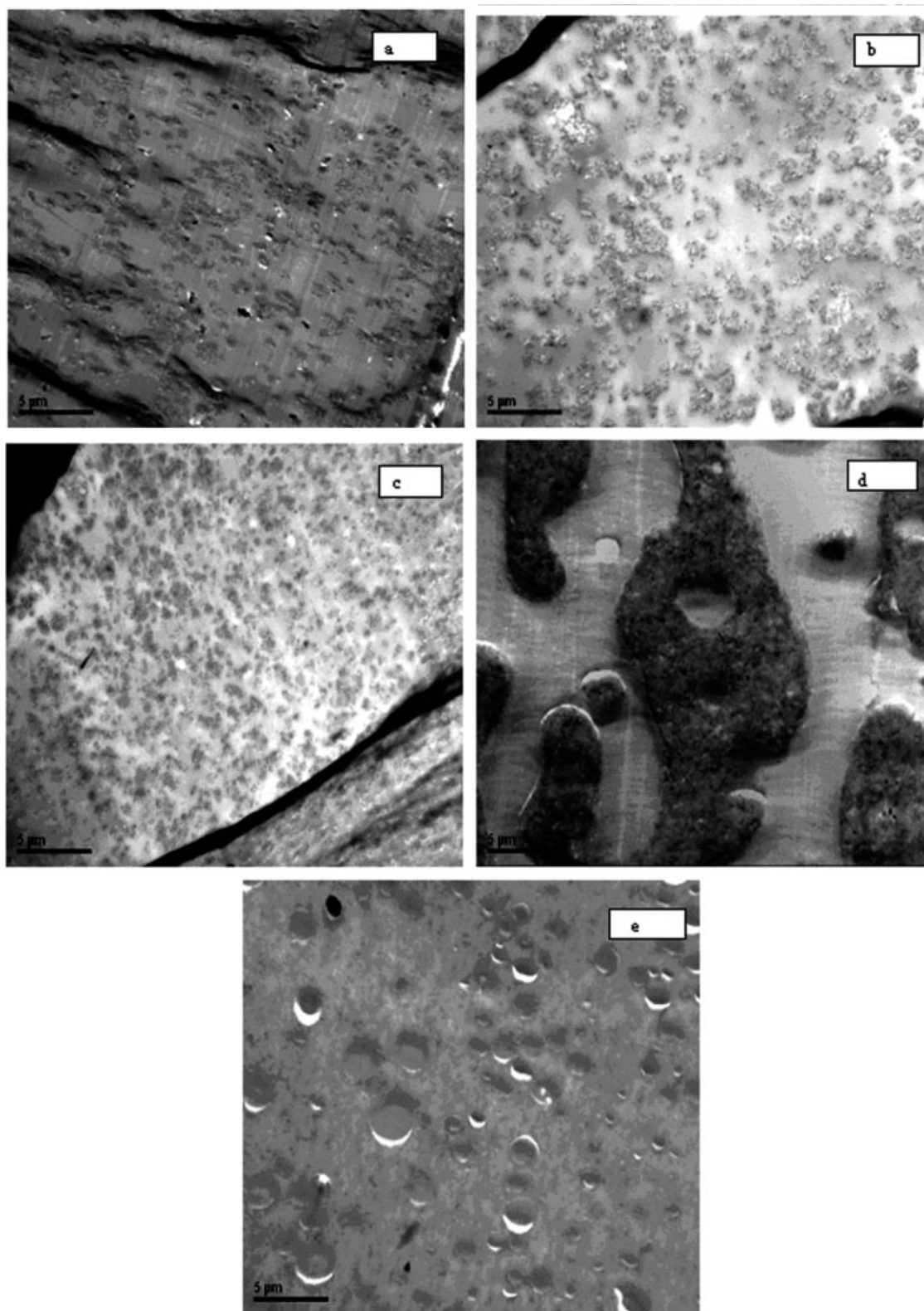
increase of CB content in PA6 phase from 4 to 18 wt %, suggesting that the percolation threshold of System II is in this range of CB content. Further increasing the CB content in PA6 phase, the electric conductivity of composites continuously increases, and then almost levels off when the CB content in PA6 phase is bigger than 20 wt %.

From Figure 2, it can be concluded that CB content in PA6 phase is an important factor affecting the electric conductivity of PS/PA6/CB composites. No matter the PA6/CB phase is continuous or dispersed, the electric conductivity of PS/PA6/CB composites gets higher with the increase of the CB content in PA6 phase. In addition, at the same CB content in PA6, the electric conductivity of composites in which PA6/CB is continuous is higher than that of composites in which PA6/CB is dispersed.

### Effect of the morphology of PA6/CB phase on the electric conductivity of PS/PA6/CB composites when CB content in PA6 is constant

Figure 3 shows the effect of the morphology of PA6/CB phase on the electric conductivity of PS/PA6/CB composites (System III) when the CB content in PA6 is constant at 23 wt %. It is clearly seen that the curve of the electric conductivity of PS/PA6/CB composites can be divided into three segments as the PA6/CB weight percent in composites reducing from about 75 to 15 wt % according to the difference of the fit relationship between the PA6/CB weight percent and the electric conductivity.

In the first segment of the curve, when the weight percent of PA6/CB phase is from 75 to 25 wt %, the PA6/CB phase is continuous, electrons can transmit in the continuous PA6/CB phase, thereby making PS/PA6/CB composites highly conductive. When the PA6/CB weight percent reduces gradually, the continuous degree of PA6/CB phase slowly decreases, and accordingly, the electric conductivity of PS/PA6/CB composites decreases slowly. When the PA6/CB weight percent further decreases from about 25 to 20 wt % (2nd segment), PA6/CB phase becomes dispersed phase from continuous phase, and the electric conductivity of composites decreases very fast because the distance between PA6/CB dispersed phase particles gets bigger and it is harder for the electron to traverse the PS phase between them. When the PA6/CB weight percent continuously decreases from about 20 to 15 wt %, the electric conductivity of the composite is very low and the composite can be taken as insulator, suggesting that when the PA6/CB weight percent is at about 15 wt % (Sample IIIj), the distance between the PA6/CB particles is the shortest distance for the electrons to transmit and thus form an electric conductive net.

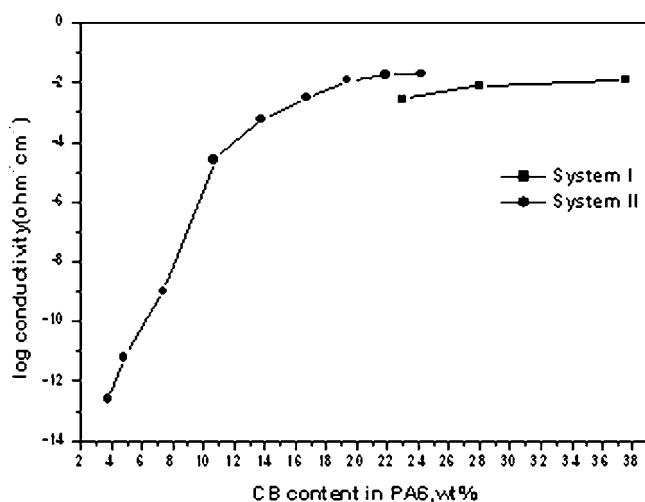


**Figure 1** TEM micrographs of various PS/PA6/CB composites: (a) PS/PA6/CB (w/w/w = 40/10/3); (b) PS/PA6/CB (w/w/w = 40/10/4); (c) PS/PA6/CB (w/w/w = 40/10/6); (d) PS/PA6/CB (w/w/w = 25/25/3); (e) PS/PA6/CB (w/w/w = 10/40/3).

We define a new term, SACD, which refers the shortest distance between PA6/CB phase particles of PS/PA6/CB composites for the electrons to transmit

and thus form an electric conductive net. For System III, its TEM pictures were shown in Figure 4, and its SACD is about 54 nm.



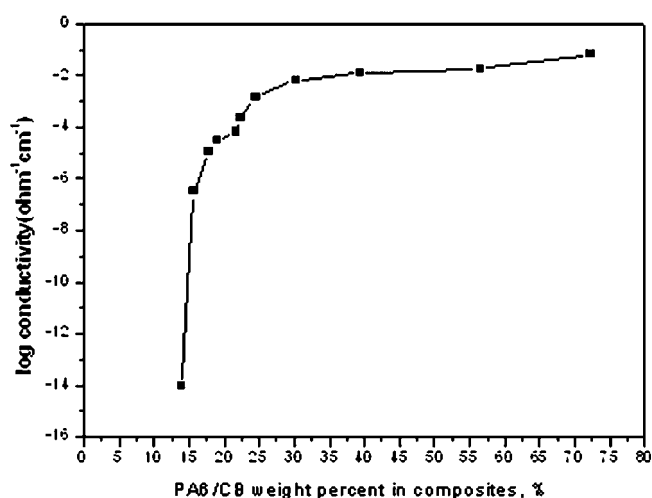


**Figure 2** Electrical conductivity of two PS/PA6/CB composites as a function of CB content in PA6 phase.

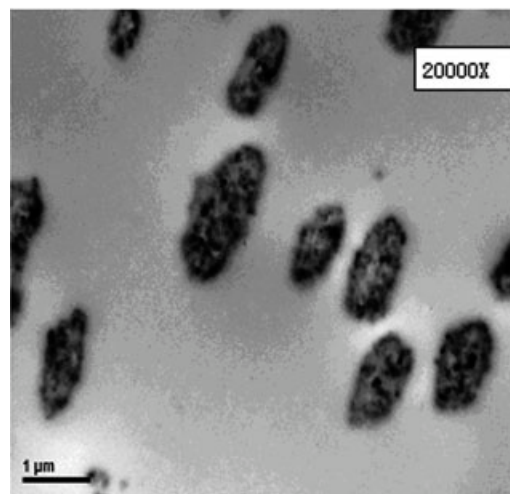
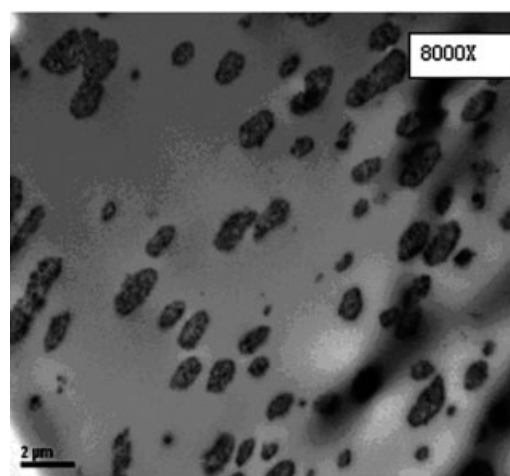
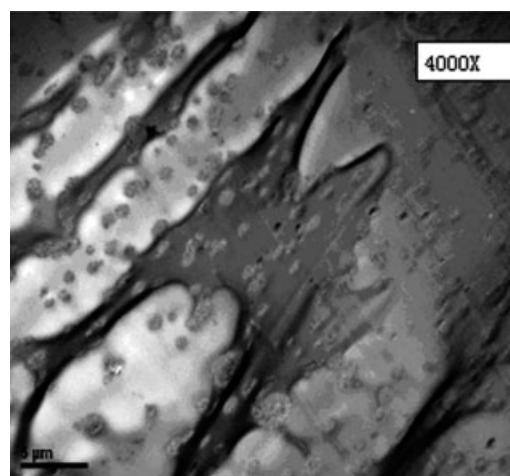
In a word, when the CB content in PA6 phase is kept constant, the morphology of PA6/CB phase is another important factor affecting the electric conductivity of the PS/PA6/CB composites. Higher continuous degree of PA6/CB phase leads to higher electric conductivity of PS/PA6/CB composites. When PA6/CB is dispersed phase, there is a SACD between PA6/CB dispersed phase particles, and only when the distances between PA6/CB particles are smaller than SACD, the PS/PA6/CB composite is electric conductive.

#### Effect of the weight ratio of PS and PA6 on the electric conductivity of PS/PA6/CB composites when the CB content in composites is constant

From the earlier discussion, we know that the best condition for the electric conductivity of PS/PA6/CB

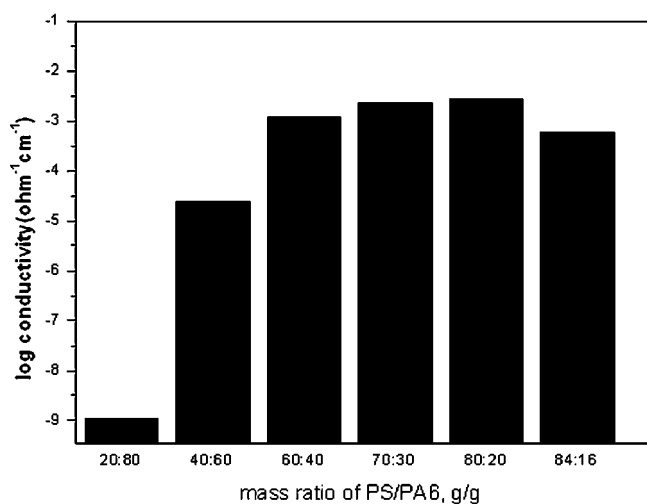


**Figure 3** Electrical conductivity of PS/PA6/CB (CB content in PA6 is 23 wt %) composites as a function of PA6/CB weight percent in composites.



**Figure 4** TEM micrographs of a PS/PA6/CB (70g/10g/3g) composite with different magnitudes.

composites is that the PA6/CB phase has the highest continuous degree and the CB content in PA6 phase is the largest. But, when the total mass of PS/PA6/CB composites and the mass of CB are constant, these two points cannot be satisfied; at the same time, by changing the mass ratio of PS and PA6, that is, to



**Figure 5** Effect of the mass ratio between PS and PA6 on the electrical conductivity of PS/PA6/CB composites with the CB content in composite at 5.67 wt %.

make the continuous degree of PA6/CB phase highest the mass ratio of PS and PA6 should be as small as possible. On the other hand, to make the content of CB largest in the PA6 phase, the mass ratio of PS and PA6 should be as large as possible. That is, making the continuous degree of PA6/CB phase highest and making the CB content largest in PA6 phase is a contravention. Hence, we can predict that there must be an equilibrium point in the competition between CB content of PA6 phase and the morphology of PA6/CB phase at which the PS/PA6/CB composites have the highest electric conductivity.

Figure 5 shows the effect of the weight ratio between PS and PA6 on the electric conductivity of PS/PA6/CB composites when the CB content in composites is constant at 5.67 wt % (System IV). It is clearly seen that PS/PA6/CB composites have the highest electric conductivity when the mass ratio of PS and PA6 is 80 : 20. From its TEM picture shown in Figure 1(a), it can be seen that the PA6/CB is dispersed phase, while in this composition, the distance between PA6/CB dispersed phase particles is small, and its CB content in the PA6 phase is as high as 23 wt %. This is optimum point at which the PS/PA6/CB composites (CB content in composites keeps

constant at 5.67 wt %) have the highest electric conductivity

## CONCLUSIONS

1. CB particles only distribute in PA6 phase in the PS/PA6/CB composites because of the strong polarity of PA6.
2. The CB content in PA6 phase and the morphology of PA6/CB phase both affect the electric conductivity of PS/PA6/CB composites. No matter the PA6/CB phase is continuous or dispersed phase, the electric conductivity of PS/PA6/CB composites gets higher as the CB content in the PA6 phase increases. When the content of CB in PA6 keeps constant, higher the continuous degree of the PA6/CB phase leads to higher electric conductivity.
3. When PA6/CB is the dispersed phase, there is a SACD between PA6/CB dispersed phase particles. Only when the distances between PA6/CB particles are smaller than SACD, PS/PA6/CB composites are electric conductive. The SACD of PS/PA6/CB composites in which CB content is 23 wt % in PA6 was quantitatively counted, which is about 54 nm.
4. Keeping the CB content in composites at 5.67 wt %, the optimum mass ratio of PS/PA6 for the composites having the highest electric conductivity is 80 : 20, resulting from the competitive result of above two factors (that is the CB content in PA6 phase and the morphology of PA6/CB phase).

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