

## Electrical Percolation of Carbon Black Filled Poly (ethylene oxide) Composites in Relation to the Matrix Morphology

Gen Shui CHENG<sup>1,2</sup>, Ji Wen HU<sup>1,2\*</sup>, Ming Qiu ZHANG<sup>2</sup>, Ming Wei LI<sup>1</sup>,  
Ding Shu XIAO<sup>1</sup>, Min Zhi RONG<sup>2</sup>

<sup>1</sup>Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650

<sup>2</sup>Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Zhongshan University, Guangzhou 510275

**Abstract:** The present work studies the electrical conduction performance of carbon black (CB) filled poly(ethylene oxide) (PEO) composites. The addition of CB leads to reduced matrix crystallinity as the fillers which are partly situated inside the lamellae and hinder the growth of PEO crystallites. As a result, the electrical percolation behavior is related with the matrix morphology.

**Keywords:** Poly(ethylene oxide), carbon black, composites, percolation, crystalline morphology.

Intensive studies have been carried out on conductive polymer composites owing to their potential applications as antistatic materials, self-regulating heaters, gas sensor, *etc.* It is found that the electrical performance of the materials is highly dependent on composites' microstructure in addition to the nature of fillers<sup>1</sup>. On the basis of this consideration, electrical percolation threshold can be adjusted either by segregated distribution<sup>2</sup> or by selective distribution of fillers<sup>3</sup> during manufacturing.

With respect to the investigation on submicron scale, conductive fillers are generally believed to be expelled to the amorphous regions among the spherulites when the matrix polymer crystallizes<sup>4</sup>. Although it has been deduced from melting behaviors of the composites that conductive fillers might also be possibly introduced into the lamella structure<sup>5</sup>, there is not any direct evidence supporting this mechanism yet. Since the dispersion status of conductive fillers in a composite is related to the environmental responses and has theoretical and practical significance, the present paper studies the conductive property of carbon black(CB) filled poly(ethylene oxide)(PEO) and the morphological variation of the matrix as a function of the filler incorporation. PEO is selected as the matrix because it has high crystallinity and crystallization rate. Talibuddin *et al.* reported that the blends of PEO and amorphous polymer with higher  $T_g$  present spherulites trapping the latter between crystal lamellae as a result of their poor mobility<sup>6</sup>. Therefore, the objective of the present work is to verify whether similar phenomenon would be observed in CB/PEO composites to be dispersed in the inter-spherulitic amorphous phases. Although the lamellar growth is not further depressed in this case, the perfection degree of the spherulites is still.

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\* E-mail: hjw@mail.gic.ac.cn

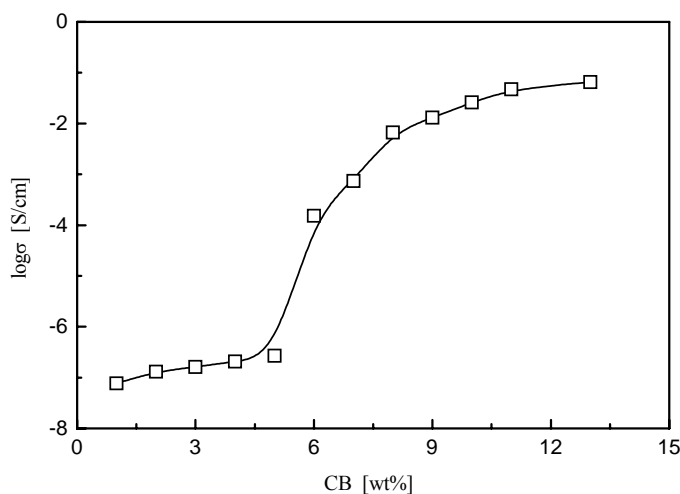
## Experimental

PEO ( $M_n=7.74\times 10^5$ ) was purchased from Fluka AG. CB (type XC-72) with primary particle size of 50-70 nm was supplied by Cabot Co. Ltd. For preparing CB/PEO composites, CB was added into 2% (w/v) solution of PEO in chloroform. After high-speed stirring, the suspension was cast on an epoxy plate with comb-like electrodes. To remove the residual solvent, the films were laid in air for 24 h and vacuum desiccated for additional 24 h. Eventually, the composite films 30~40  $\mu\text{m}$  thick were annealed at 36  $^\circ\text{C}$  for 48 h. Room temperature dc conductivity was measured at a relative humidity of 65%. Wide angle X-ray diffraction (WAXD) studies were performed on a Rigaku D/max-1200 X-ray diffractometer at a scanning rate of 3 degree/min, employing nickel-filtered Cu ( $K_\alpha$ ) radiation at voltage of 40 kV and current of 30 mA.

## Results and Discussion

It can be seen from **Figure 1** that the conductivity at CB loading lower than 5wt% ranges from  $10^{-6}$  to  $10^{-7}$  S/cm, which is significantly higher than the systems of CB/high density polyethylene (HDPE)<sup>7</sup> and CB/polypropylene (PP)<sup>8</sup>. It can be attributed to the presence of polar groups of PEO, as an enhanced conductivity of conductive composites has been correlated with the increased polarity of the repeated units of the matrix<sup>9</sup>. According to the peak position of the drastic increase of conductivity with respect to CB content, it is known that the percolation threshold of the CB/PEO composites lies in about 6wt%. In accordance with **Figure 1**, WAXD analysis of the composites was also carried out (**Table 1**). With a rise in CB concentration the values of diffraction angle  $2\theta$  and lattice distance of PEO crystallites almost keep unchanged, meaning that the crystalline structure of PEO is not affected. That is, CB was not squeezed into the crystal lattices of PEO.

**Figure 1** Electrical conductivity,  $\sigma$ , of CB/PEO composites as a function of CB content.



However, it is interesting to note that the matrix crystallinity decreases remarkably with increasing CB content. To further understand the related microstructural information, the stack height of basal planes of the PEO crystalline structure,  $L_c$ , should be estimated from the Scherrer equation. Since (120) plane acts as the most probable fold for PEO lamellae<sup>10</sup> and gives the strongest reflection in the WAXD spectra,  $L_c$  in the direction perpendicular to this plane gives a measure of the crystal thickness (*i.e.*,  $c$ -axis).

It is seen from **Table 1** that the  $L_c$  value of PEO decreases with CB loading and reaches the minimum at 5wt% of CB, which is close to the aforesaid percolation threshold. Further rise in CB content leads to significant changes of the lamellar thickness. Evidently the phenomenon is indicative of the hindrance effect of CB on the growth of PEO crystals. Owing to the fast crystallization habit of PEO and the reduced mobility of the fillers, some CB particles have to reside in the interlamellar regions and cannot completely diffuse from the growth front<sup>6</sup>. As a result, the development of PEO lamellar thickness is obstructed. The more CB is added, the thinner the lamellar is. When the CB content is higher than the percolation threshold, the spaces among crystal lamellae are no longer large enough to trap the CB particles. Most of the fillers have affected by the fillers. This accounts for the unchanged  $L_c$  and the continuous decrease of the matrix crystallinity with a rise in CB content over the percolation threshold. As the fillers situated in the interlamellar regions cannot join in the conduction paths and only those distributed in the amorphous regions contribute to the composites conductivity, the present CB/PEO has higher percolation threshold than CB/HDPE and CB/PP composites, in which there are no volume-filling spherulites<sup>7,8</sup>.

## Conclusion

By using solution blended CB/PEO composites as model materials, it is proved that the conductive fillers can reside inside the lamellae of PEO crystallites and greatly influence the crystalline structure of the matrix. In the case of higher CB content, especially when CB content exceeds the percolation threshold, this effect becomes less significant.

**Table 1** Structural parameters of PEO yielded from (120) WAXD reflections.

CB content (wt%)	$2\theta$	Lattice distance (nm)	Crystallinity (%)	$L_c$ (nm)
0	18.9	0.47	78	30.1
3	19.2	0.46	66	27.0
5	19.3	0.46	62	23.0
6	19.1	0.46	61	23.1
8	19.2	0.46	60	23.2
11	19.1	0.46	59	23.0

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