

Development of Electronic Packages from Polypropylene/Ethylene Propylene Rubber Blends: A Double Percolation Approach

Sarote PHROMDEE¹, Parkpoom LORJAI², Sunan TIPTIPAKORN³ and Sarawut RIMDUSIT^{1*}

¹Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand

²Process Technology Research Department, PTT Research and Technology Institute, Wangnoi, Ayutthaya 13170, Thailand

³Department of Chemistry, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen, NakornPathom 73140, Thailand

Abstract

Volume resistivity of less than $10^4 \Omega \cdot \text{cm}$ is required for typical electrically conductive packages. Conductive polypropylene (PP) packages with the above level of conductivity value can be achieved by a use of carbon black (CB) as conductive filler. One promising method to reduce the amount of conductive fillers in composites is to use immiscible or partially miscible polymer blends. The phenomenon is known as a double percolation behavior. In this work, electrically conductive composite packages were prepared from polymer blends of PP and ethylene propylene rubber (EPR) with CB as conductive filler (PP/EPR/CB). PP/EPR mixtures at the weight ratios between 100/0 to 50/50 were blended with CB as conductive filler ranging from 0 to 30 wt% by melt mixing in an internal mixer at 200 °C for 10 min, followed by compression molding at the same temperature. The blends evidently provided a reduced percolation threshold with the electrical conductivity values greater than those of the CB filled PP composites. To achieve the volume resistivity of $10^4 \Omega \cdot \text{cm}$, the CB content in the blend can be reduced at least 50% compared to the composite using neat PP as a matrix. Scanning electron microscopy has been used to verify the preferential location of the conductive particles and to reveal the complex morphology developed. The results presented in this study show the possibility of specially designed polymer compositions for conductive applications.

Keywords : Conductive Polymer Composite, Carbon Black, Percolation Threshold, Electrical Properties

DOI : 10.14456/jmmm.2014.6

Introduction

Synthetic polymers are often very good electrically insulating materials and in order to make them conduct electricity, the preferred choice is to mix them with conductive fillers, like carbon black, graphite, carbon fibers, carbon nanotubes, metal particles, etc. Traditionally CB is the filler of choice for large-scale industrial processes, especially for cost reasons, and its addition to the polymer matrix can lead to a degree of electrical conductivity⁽¹⁾. Packaging materials are classified into conductive, static dissipative and insulative according to their volume/ surface resistivity. According to the electronic industry association (EIA) and the electrostatic discharge association (ESDA) standards, static dissipative material volume resistivity is in the range of 10^4 – $10^{11} \Omega \cdot \text{cm}$ ⁽²⁾. Materials with resistivities higher or lower than this range are considered insulator or conductor, respectively.

For CB-filled conducting polymer composites, it is desirable to decrease a percolation threshold as low as possible. Concerning how to reduce the percolation threshold and how to control the desired conductivity of the CB-filled polymer composites, most studies focus on the optimization of morphology of the matrix apart from CB structure and polymer characteristics. In terms large-scale practical applications, melt processing, the addition of CB in the single thermoplastic polymeric hosts is interested. However, in most of these systems, the percolation threshold remains high because of the high filler content. This system leads to difficulties in processing due to an increase in melt-viscosity of the blends, the high final cost and, poor mechanical properties, such as brittle. To maintain processability of conductive polymer composites with low cost, minimal amount of carbon black is preferable in the conductive composites. By introducing a second polymer with

immiscible or partially miscible nature to the first polymer, and if the conductive filler is localized in one polymer phase, a system of double percolation with minimal filler content can be achieved⁽²⁻⁵⁾.

In this research, CB filled polymer blends consisting of PP and EPR were investigated. The PP/EPR/CB composites with varied compositions were prepared by melt-mixing method. The CB distribution in the blends and the relationship between the morphology and electrical properties of the blends were studied.

Materials and Experimental Procedures

Materials

PP with a low melt flow index and EPR with a high melt flow index were produced by IRPC Co., Ltd., Thailand. Electrically conductive CB (low structure type) was provided by TIMCAL Co., Ltd., with specific surface area of 65 m²/g, and mean particles diameter of 45 nm.

Sample preparation

PP and EPR were melt mixed with the conductive CB in an internal mixer at 200°C and 40 rpm for 15 minutes. Blends were then compression molded at 15 MPa and 200 °C in a mold 100 × 100 × 2 mm³ for 10 min. After being cooled to room temperature in air, the composite sheets were removed and cut into test samples. The weight ratios of PP/EPR ranged from 100/0 to 50/50 were used in order to keep EPR as the minor phase, and the CB content was 0-30 wt%.

Characterization

An Electrometer (4284A, HP) was used to perform room-temperature resistivity measurements on samples with resistivity lower than 10⁶ Ω cm, while a high-resistance meter (6517A, Keithley) was used for samples with higher resistivity.

Samples were fractured in liquid nitrogen, the fracture surfaces were coated with Au and their morphologies were observed by scanning electron microscopy (SEM; JHM-5410LV, JEOL).

Results and Discussion

Electrical properties of CB in neat PP and EPR

It is well recognized that PP and EPR are insulating polymer, however, the electrical conductivity of these polymers can be achieved by

dispersing conductive filler, e.g., carbon black (CB), throughout the polymer matrix. The critical amount of filler necessary to build up a continuous conductive network and to make the material conductive is referred to as the percolation threshold. This concentration at which the insulator polymer becomes conductive is an important factor to determine the minimum CB content required in preparing conductive compound.

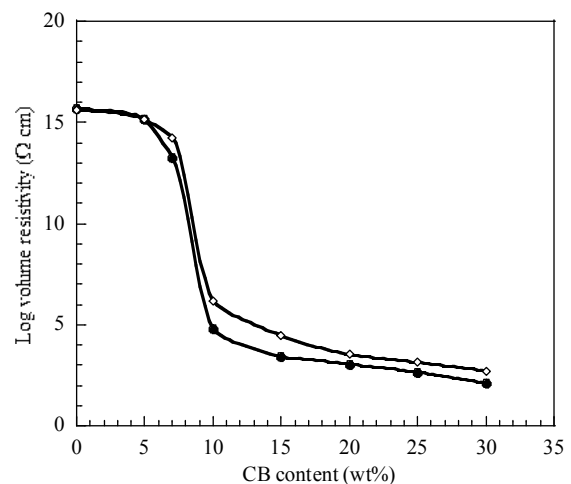


Figure 1. Volume resistivity of CB-filled PP and EPR at various CB contents: (●) PP and (◇) EPR.

The volume resistivity of the PP and EPR was plotted against the CB contents as shown in Figure 1. PP and EPR are insulator with a volume resistivity in the order of 10¹⁶ Ω.cm. A percolation threshold, a drastic decrease in volume resistivity, exist where the volume fraction of CB becomes sufficient to provide continuous electrical paths through the polymer. The percolation threshold of CB-filled polymers was determined at the volume fraction of CB that the compounds change from insulative (>10¹¹ Ω.cm) to conductive (< 10⁴ Ω.cm)⁽²⁾. It was observed that the percolation threshold of PP and EPR are about 6-13 wt% CB.

Electrical properties of CB-filled PP/EPR blends

An addition of CB to PP/EPR blend is considered, the percolation threshold depends strongly on the phase morphology and the distribution of CB in the polymer blends. Figure 2 shows the volume resistivity curves of PP/EPR blends at the weight ratios from 100/0 to 50/50 with CB as conductive filler ranging from 0 to 30 wt%. The percolation regions of the PP/EPR-based composites were lower than those of PP-based composites and they were shifted to the left.

For example, PP/EPR mixtures at the weight ratios between 80/20 and 50/50 were blended with CB content of 10% provided a volume resistivity of about 3 order Ωcm , which was a much lower CB content than that of the PP/CB systems at the same volume resistivity. The percolation threshold was observed at about 2-6 wt% of CB content, where the volume resistivity changed by 11 orders of magnitude. As shown in Figure 2, an interesting phenomenon is found in the electrical properties of CB-filled PP/EPR blend ratio of 90/10. The percolation threshold is about 6-13 wt% CB, which is dramatically higher than that of the other PP/EPR blends. For the PP/EPR blend ratio of 90/10, PP form continuous phase and minor EPR form dispersed phase. If the CB selectively disperses in the PP phase, the CB content would reach the percolation threshold of PP and lead to conductive composite⁽⁴⁾. However, the CB content at which percolation commences is lower in the polymer blend composite than in the single polymer composite. This is due to double percolation occurring due to the CB having a heterogeneous distribution in one phase of the blended matrix^(5,6).

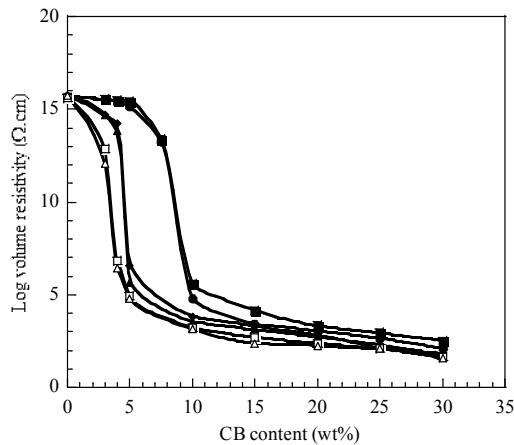


Figure 2. Volume resistivity of CB-filled PP and PP/EPR blends at various ratios: (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, (□) 60/40 and (△) 50/50.

Morphologies of the composites

The morphologies of PP/EPR blends are shown in Figures 3a-3f. The weight ratios are 0%, 10%, 20%, 30%, 40%, and 50% EPR in PP, respectively. The morphology in Figures 3a-3c shows discrete domains of EPR in a matrix of PP with domain shape becoming less regular with increasing fraction of EPR. The co-continuous phase of PP and EPR was observed in the PP/EPR blends at EPR content higher than 30 wt% (Figures 3d-3f).

Figures 4a-4f show the morphologies of 5 wt% CB-filled PP/EPR blends with various ratios. For the CB-filled PP/EPR blends between 60/40 and 50/50, the addition of CB led to EPR phase mainly form continuous structure. Both PP and CB in the EPR phase formed continuous phases in three-dimensional space; such structures are known as co-continuous phase structures.

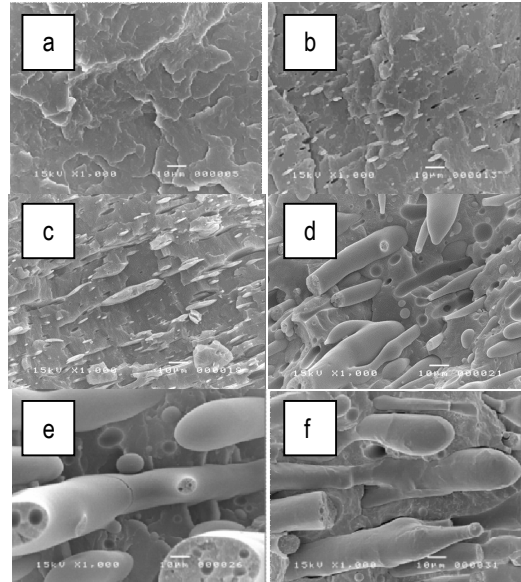


Figure 3. SEM micrographs of freeze-fracture surface of PP/EPR blend at various blend ratios: (a) 100/0 (b) 90/10 (c) 80/20 (d) 70/30 (e) 60/40 and (f) 50/50.

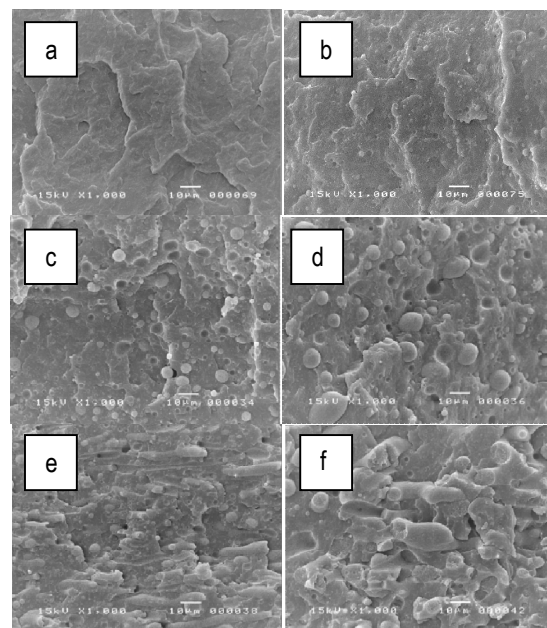


Figure 4. SEM micrographs of freeze-fracture surface of 5 wt% CB-filled PP/EPR blend at various blend ratios: (a) 100/0 (b) 90/10 (c) 80/20 (d) 70/30 (e) 60/40 and (f) 50/50.

Additionally, the different distribution of CB in PP domains as well as CB in EPR domains in PP/EPR blend at a fixed blend ratio of 60/40 with 5 wt% CB can be evidently observed in Figure 5. This selective distribution of CB in the EPR phase is attributed to its lower interfacial free energy, crystallinity, and viscosity compared to PP phase.

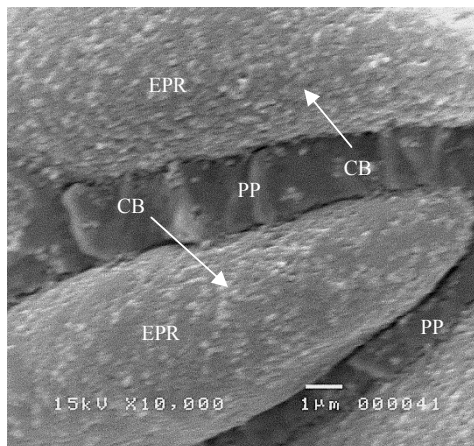


Figure 5. SEM micrographs of freeze-fracture surface of 5 wt% CB-filled PP/EPR blend ratio of 60/40.

Conclusions

CB-filled PP/EPR blends afforded lower filler contents to provide the same volume resistivity than CB-filled PP, i.e. to achieve the volume resistivity less than $10^4 \Omega \cdot \text{cm}$, the CB contents of 15wt% and ca.6 wt% were required to fill in PP and PP/EPR blends, respectively. In addition, the percolation threshold of the obtained CB-filled PP/EPR blends were approximately 2-6 wt% of CB while CB-filled PP was about 6-13 wt% of CB. The CB content in the blends can be reduced at least 50% compared to the composite using neat PP as a matrix.

SEM micrographs reveal that PP/CB and PP/EPR/CB composites have different microstructures. The PP/EPR blends create a multiple phase system in which the conductive filler exhibits preferential localization in the EPR phase.

Acknowledgements

This work is supported by PTT Public Company Limited for financial support, National Research University (WCU-028-AM-57) and partially funded by the Ratchadaphiseksomphot Endowment Fund of Chulalongkorn University (RES560530007-AM). In addition, the financial supported by Thailand Research Fund (TRF)-(MRG5680029) was also acknowledged.

References

1. Gkourmpis, T., Svanberg, C., Kaliappan, S. K., Schaffer, W., Obadal, M., Kandioller, G., and Tranchida, D. (2013). Improved electrical and flow properties of conductive polyolefin blends : Modification of poly(ethylene vinyl acetate) copolymer/carbon black with ethylene-propylene copolymer. *Eur. Polym. J.* **49** : 1975-1983.
2. Al-Saleh, M. H. and Sundararaj, U. (2008). An innovative method to reduce percolation threshold of carbon black filled immiscible polymer blends. *Compos. Part A : Appl. Sci. Manuf.* **39(2)** : 284-293.
3. Thielen, A., Valange, B., and Viering, S. (2001). *Conductive polymer blends with finely divided conductive material selectively localized in continuous polymer phase or continuous interface.* in United States Patent, Boston : Cabot Corporation.
4. Cui, L.M., Zhang, Y., Zhang, Y.X., Zhang, X.F., and Zhou, W. (2007). Electrical properties and conductive mechanisms of immiscible polypropylene/Novolac blends filled with carbon black. *Eur. Polym. J.* **43** : 5097-5106.
5. Shen, L., Wang, F. Q., Yang, H., and Meng, Q. R. (2011) The combined effects of carbon black and carbon fiber on the electrical properties of composites based on polyethylene or polyethylene/ polypropylene blend. *Polym. Test.* **30(4)** : 442-448.
6. Feng, J.Y., Chan, C.M., and Li, J.X. (2003). A method to control the dispersion of carbon black in an immiscible polymer blend. *Polym. Eng. Sci.* **43(5)** : 1058-1063.