

Explaining electrical resistivity effects in electro-conductive polymer composites

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Morphological analysis of saponified carbon-black-filled semi-crystalline polymers provides a new theory for positive and negative temperature coefficient phenomena.

The unique combination of electro-conductive polymer composite properties (i.e., metallic conductivity and polymer properties) means that they are becoming increasingly useful in a variety of applications (e.g., heating elements, temperature sensors, and current limiters).^{1–8} These composites usually consist of a thermoplastic matrix and dispersed electro-conductive fillers, e.g., carbon black (CB) powder. CB-filled semi-crystalline polymer composites usually exhibit two insulator–conductor transitions. The first of these is the dependence of electrical resistivity on filler content, i.e., that there is a critical concentration (the percolation threshold) of fillers necessary to form a continuous conductive network.⁹ The second phenomenon is the temperature dependence of electrical resistivity in these composites. Known as the positive temperature coefficient (PTC) effect, this is the sharp increase in electrical resistivity with temperature that occurs close to the melting point (T_m) of the crystalline polymer.¹⁰ Negative temperature coefficient (NTC) effects are also observed, but these do not have any impact on the PTC phenomenon. Although several theories have been proposed to explain the PTC and NTC effects of CB-filled semi-crystalline polymer composites, these do not provide a satisfactory explanation of experimental results.^{10–12}

It is generally thought that the PTC effect in CB-filled semi-crystalline polymer composites is caused by the breakup of the electro-conductive network during sample heating.^{10–12} It has been attempted, in previous efforts, to elucidate which specific parameter (e.g., thermal expansion, electron tunnel effect, electric field emission, or inner stress) undergoes the non-linear shift in resistivity with increasing temperature. Yet there are remaining problems with the proposed theories, and the mechanism responsible for the PTC phenomenon still needs to be properly established.¹⁰

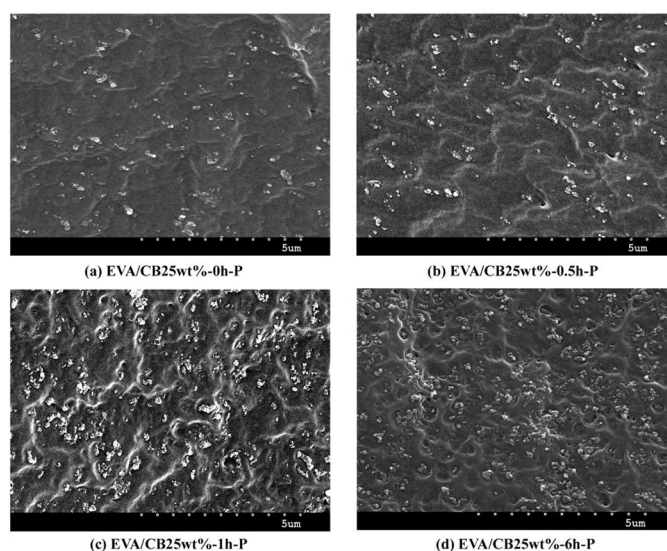


Figure 1. Scanning electron microscope (SEM) images of cryogenically fractured surfaces of carbon black (CB)-filled semi-crystalline polymer composites. The thermoplastic matrix in these composite samples is poly(ethylene-co vinyl acetate), EVA. These composites were produced with the suspension precipitation saponification (P) method. All four samples had CB loadings of 25wt%. The range in saponification time (0–6 hours) produced different crystallinity (χ_c) values for each sample: (a) 9.4%, (b) 9.9%, (c) 12.4%, and (d) 15.1%.

In this study, we have prepared a set of saponified electro-conductive composites that are made from poly(ethylene-co-vinyl acetate)—EVA—and CB particles.¹³ We use two different methods—solvent-casting saponification (D) and suspension precipitation saponification (P)—with CB loadings of 5–25wt% to make these samples. We also obtained scanning electron microscope (SEM) images of the samples so that we could evaluate the morphology, electrical resistivity, thermal, and mechanical properties of the composites and thus propose a new explanation for the PTC effect.

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An SEM image of our EVA/CB25wt%-P sample—see Figure 1(a)—shows smooth fracture surfaces, with weaker plunging crevasses. In samples produced with longer saponification times, we observe a variety of different morphologies. At first—see Figure 1(b)—much deeper plunging crevasses appear. Next, as shown in Figure 1(c), wavelike ambiguous cavities can be easily discerned. Finally—see Figure 1(d)—oval cavity structures are formed. The increase in the crystallinity of the EVA matrix after saponification can induce an enhanced conduction path by way of CB rejection into the amorphous regions. This increases the relative CB content in the amorphous phase and improves the conducting networks.¹⁴

We also prepared, and imaged, a set of electro-conductive composites that contain different polymer matrix materials (see Figure 2). The SEM images for our silicone rubber/CB composite—see Figure 2(a)—and the EVA/CB composite—see Figure 2(b)—show that CB particles are detached from the polymer matrix and are randomly dispersed. In the high-density polyethylene (HDPE)/CB—see Figure 2(c)—and polyvinylidene fluoride (PVDF)/CB—see Figure 2(d)—composites, which have higher crystalline content than the EVA/CB sample, the

CB aggregates are usually located in oval cavities that are larger than the particles themselves.¹²

We are able to use our morphological analyses of the different composite systems as a basis for a detailed explanation of the PTC and NTC mechanisms that occur in CB-filled semi-crystalline polymer composites. We find that the electro-conductive particles beyond the percolation threshold mainly exist in amorphous regions. These are separated by crystalline films that are more electro-conductive than amorphous films. When a thin, insulating polymer layer separates the filler particles, the electro-conductivity is dominated by charge transport (via the tunneling effect).^{15,16} As the temperature increases and approaches the T_m of the polymer matrix, the crystals start to melt. This leads to the formation of new amorphous regions. Melting of the polymer crystals also causes thermal expansion, and the gaps between CB particles in the polymer matrix broaden greatly. This causes the resistivity of the electro-conductive composites to increase rapidly.¹² In addition, the migration of the CB particles into the previously CB-free crystalline region causes the concentration of the filler in the matrix to be further diluted. As a result, CB particles are mostly trapped inside the polymer matrix and are randomly dispersed, as shown in Figure 2(b). These trapped filler particles are coated with a sheath of polymer, which inhibits electrical conduction through the filler network.

In contrast, at temperatures beyond T_m , the filler particles can penetrate the softened polymer matrix and easily form networks. This results in re-aggregation of CB particles, i.e., in a van der Waals-like interaction between the filler particles. The fracture surfaces shown in Figure 1(a) differ greatly from the solvent-casting sample—see Figure 1(b)—which appear to have many more CB aggregates and better formed electro-conductive network morphologies. We attribute this to the migration of CB particles during the precipitation process, which ensures a low viscosity of the polymer matrix. This results in the formation of new electro-conductive filler particle chains. In this case, the electro-conductivity is dominated by contact resistance that occurs between filler particles. It is also dominated by charge transport through the filler phase, which takes place via direct contact between the particles. A final rapid decrease in the resistivity (i.e., the NTC effect) is caused by the formation of a highly electro-conductive flocculated structure. This occurs when the viscosity of the polymer is sufficiently low, i.e., at high temperatures.¹⁷

In this work, we have evaluated the morphological, electrical resistivity, thermal, and mechanical properties of CB-filled semi-crystalline polymer composites. We have used the results of our analyses to propose a new explanation for PTC and NTC effects that are observed in saponified EVA/CB composites. To produce composites that are reproducible, a high PTC effect is required to prevent the material from

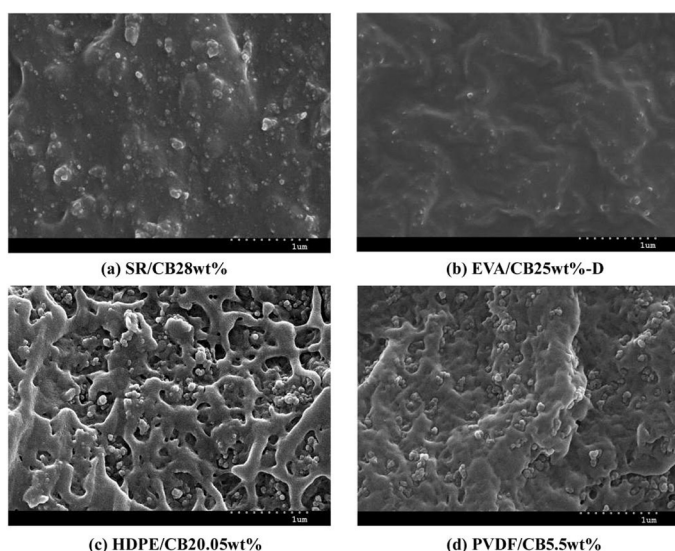


Figure 2. SEM images of cryogenically fractured surfaces (above the percolation threshold) of CB-filled electro-conductive polymer composites with different matrix materials. (a) Silicone rubber matrix, with a CB loading of 28wt%. (b) EVA matrix, with a CB loading of 25wt% and χ_c of 8.1%. This composite was produced using the solvent-casting saponification (D) method. (c) High-density polyethylene (HDPE) matrix, with a CB loading of 20.05wt% and χ_c of 45.4%. (d) Polyvinylidene fluoride (PVDF) matrix with a CB loading of 5.5wt% and χ_c of 58.7%.

overheating. In addition, a relatively low room temperature resistivity is needed to ensure sufficient thermal output. Compared with crystalline PTC plastics, rubbery PTC materials can easily form cross-linking fabrics that prevent the NTC effect (but while maintaining rubbery toughness, processability, and moldability). In our future studies, we will focus on evaluating the effect of morphology on the electric conductivity and PTC reproducibility of binary rubber blend systems that are filled with CB particles.

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References

1. R. H. Norman, **Conductive Rubbers and Plastics: Their Production, Application and Test Methods**, p. 277, Elsevier, 1970.
2. D. M. Bigg, *Mechanical, thermal, and electrical properties of metal fiber-filled polymer composites*, **Polym. Eng. Sci.** **19**, pp. 1188–1192, 1979.
3. J. Kost, M. Narkis, and A. Foux, *Resistivity behavior of carbon-black-filled silicone rubber in cyclic loading experiments*, **J. Appl. Polym. Sci.** **29**, pp. 3937–3946, 1984.
4. E.-S. Park, S.-J. Yun, G.-T. Kim, I.-J. Park, W.-H. Choi, J.-W. Jeong, S.-Y. Hong, H.-W. Park, L. W. Jang, and J.-S. Yoon, *Preparation of positive-temperature coefficient heaters using platinum-catalyzed silicone rubber*, **J. Appl. Polym. Sci.** **92**, pp. 1611–1617, 2004.
5. E.-S. Park, L. W. Jang, and J.-S. Yoon, *Resistivity and thermal reproducibility of carbon black and metallic powder filled silicone rubber heaters*, **J. Appl. Polym. Sci.** **95**, pp. 1122–1128, 2005.
6. E.-S. Park, *Resistivity and thermal reproducibility of carbon black and SnO₂/Sb coated titanium dioxide filled silicone rubber heaters*, **Macromolec. Mater. Eng.** **290**, pp. 1213–1219, 2005.
7. E.-S. Park, *Resistivity and thermal reproducibility of high-density polyethylene heaters filled with carbon black*, **Macromolec. Mater. Eng.** **291**, pp. 690–696, 2006.
8. E.-J. Lee, J.-S. Yoon, and E.-S. Park, *Morphology, resistivity, and thermal behavior of EVOH/carbon black and EVOH/graphite composites prepared by simple saponification method*, **Polym. Compos.** **32**, pp. 714–726, 2011.
9. H. Pang, Y.-C. Zhang, T. Chen, B.-Q. Zeng, and Z.-M. Li, *Tunable positive temperature coefficient of resistivity in an electrically conducting polymer/graphene composite*, **Appl. Phys. Lett.** **96**, p. 251907, 2010. doi:10.1063/1.3457170
10. H. P. Xu, Y. H. Wu, D. D. Yang, J. R. Wang, and H. Q. Xie, *Study on theories and influence factors of PTC property in polymer-based conductive composites*, **Rev. Adv. Mater. Sci.** **27**, pp. 173–183, 2011.
11. H. Pang, Q. Y. Chen, Y. Bao, D. X. Yan, Y. C. Zhang, J. B. Chen, and Z. M. Li, *Temperature resistivity behaviour in carbon nanotube/ultrahigh molecular weight polyethylene composites with segregated and double percolated structure*, **Plast. Rubber Compos.** **42**, pp. 59–65, 2013.
12. Y. S. Jong, S.-H. Han, and E.-S. Park, *Effects of thermal aging on morphology, resistivity, and thermal properties of extruded high-density polyethylene/carbon black heating elements*, **Polym. Compos.** **32**, pp. 1049–1061, 2011.
13. E.-J. Lee and E.-S. Park, *Morphology, resistivity, and PTC behavior of EVOH/CB composites prepared by solvent-casting saponification and precipitation saponification*, **Polym. Compos.**, 2015. doi:10.1002/pc.23714
14. S. H. Foulger, *Reduced percolation thresholds of immiscible conductive blends*, **J. Polym. Sci. Part B: Polym. Phys.** **37**, pp. 1899–1910, 1999.
15. K. Ohe and Y. Naito, *A new resistor having an anomalously large positive temperature coefficient*, **Jpn. J. Appl. Phys.** **10**, pp. 99–108, 1971.
16. J. Meyer, *Glass transition temperature as a guide to selection of polymers suitable for PTC materials*, **Polym. Eng. Sci.** **13**, pp. 462–468, 1973.
17. M. Narkis and A. Vaxman, *Resistivity behavior of filled electrically conductive crosslinked polyethylene*, **J. Appl. Polym. Sci.** **29**, pp. 1639–1652, 1984.