Effect of Crosslinking on Carbon Black/Polyethylene Switching Materials

Electrical conductivity in insulating polymeric materials can be achieved by incorporation of dispersible conducting fillers.[1-5] Carbon black, a common conducting filler for elastomers and plastics, can impart antistatic and semiconducting properties to these materials depending on the specific type and its concentration. The electrical conductivity of carbon black is influenced by its particle size, aggregate shape and structure, porosity, and surface chemistry. The electrical conductivity of carbon black/polymer mixtures depends also on polymer characteristics such as chemical structure and crystallinity, and on processing methods and processing conditions. Improved conductivity of polymer/carbon black mixtures is achieved by using carbon black of smaller particle size (larger surface area), lower particle density (higher particle porosity), higher structure (better aggregation), and low volatility (fewer chemisorbed oxygen groups). Conductive carbon blacks such as Vulcan XC72 (Cabot Corp., MA) and Ketjenblack EC (Akzo Chemie, The Netherlands) having small particle size (~300 Å) owe their higher conductivity to both high structure and low particle density (XC-72) and to extremely low particle density (EC), respectively.

Systems of carbon black/polyethylene mixtures show a sharp resistivity increase with rise in temperature in the polymer melting region (PTC, positive temperature coefficient) followed by rapid resistivity decrease (NTC, negative temperature coefficient).[1,2,5] PTC materials having switching properties (significant resistivity increase) can be utilized in self-controlled heaters, current limiters, sensors, etc.[2]

The PTC effect can be at least partly explained by rapid expansion of the system undergoing melting, thereby increasing the gaps between particles and aggregates and thus hindering the process of electron tunneling. The ratio of crystalline to amorphous material constituting these gaps decreases with progress of the melting process, causing additional resistance in them (amorphous polymer being less conductive than its counterpart crystalline form[6]). Another factor which needs consideration is the fine distribution of the particles or aggregates in a semicrystalline polymer. An inhomogeneous distribution is expected[6] since carbon particles have been preferentially rejected from spherulites during their formation and growth. The distribution inhomogeneity depends on many factors such as size, shape, and concentration of the carbon black and upon cooling conditions of the samples from the melt. Upon heating, the "frozen" distribution of the conducting particles will start to change in the vicinity of the commencement of the melting region by movements of carbon particles. As more crystallites melt, and the viscosity is reduced with rise in temperature, an enhanced redistribution process is taking place toward a more uniform distribution permitting more and more particles or aggregates to participate in the conduction process. The NTC phenomenon is presumably caused by movements of the conducting particles in the molten polymer and formation of a new distribution of better uniformity and conductivity. If this model were true, then by arresting the particles from moving above the polyethylene melting range, the NTC phenomenon should be eliminated. From the practical point of view the NTC effect is obviously a great disadvantage since the PTC effect imparting switching properties to the compounds is losing its significance once followed by a distinguished NTC process.

A system of carbon black-filled polyethylene is thus changing its structure and distribution of the conducting particles if thermally cycled in a temperature range including the polymer melting region. The lack of reproducibility of the resistivity–temperature curve in long-term cycling and heating is thus obvious.

The experimental data combined with the theoretical considerations have led the authors to conjecture that compounds of carbon black with thermoplastic polyethylene are of little concern for practical electrical applications. Whereas carbon black has only low interaction with polyethylene, its particles are strongly attached to a crosslinked polyethylene network. The attached particles cannot be separated from the network even by refluxing in a boiling solvent for many hours at a temperature well above the melting region of the crosslinked polyethylene. Crosslinking is expected to reduce dramatically the freedom of movement of the carbon particles at high temperatures and thus to eliminate practically the NTC effect and greatly improve the reproducibility.

Polyethylene can be crosslinked either chemically or by irradiation. While irradiation crosslinking takes place at room temperature, chemical crosslinking is achieved in a molding operation at a

temperature above the polyethylene melting region, depending specifically on the decomposition kinetics of the crosslinking peroxide.   Crosslinking procedures are described in previous publications.[7] The degree of crosslinking is determined in a gel test, namely, the polymer fraction that does not dissolve in a hot boiling solvent.   Increasing concentrations of the peroxide result in higher gel contents.

The effect of crosslinking on resistivity–temperature curves is shown in Figure 1 for a crosslinked HDPE containing conductive carbon black which does not interfere with the crosslinking reaction. As can be seen, the PTC intensity (resistivities ratio, peak to room temperature) is only slightly decreased for the two extreme cases, namely, the thermoplastic mixture and its well-crosslinked counterpart (about 75% gel, same carbon black content).   The resistivity of the semicrystalline compounds (below ~110°C) increases slightly with the degree of crosslinking (DOC) as shown, while the NTC intensity (resistivities ratio, peak to resistivity at 160°C) decreases dramatically and practically vanishes in a well-crosslinked sample.

It is thus shown that with certain conductive carbon blacks, such as Ketjenblack EC (concentration range 2–6% by volume), it is possible to practically eliminate the NTC effect by proper crosslinking without sacrificing much of the PTC intensity.   This result supports the theory that structural changes in the melt are the cause for the NTC effect.   The degree of crosslinking in the range studied (0–80% gel) has no practical effect on the peak temperature and on the melting curve (120–140°C), showing that the crosslinking effect on the degree of crystallinity is practically insignificant.   The general behavior shown in Figure 1 will be retained for different concentrations of the conductive black, and only the PTC, NTC intensities will change depending on the specific concentration.   Such a behavior may not be valid for other blacks such as MT black (Vanderbilt, CT).   Such blacks also do not interfere with the crosslinking reaction; however, crosslinking may change dramatically the PTC intensity (compared to the thermoplastic counterpart) contrary to Figure 1, while the NTC behavior will conform to this figure.

The expansion/contraction processes accompanying a heating/cooling cycle cause movements of particles and their aggregates without returning to their original positions.   The phenomenon is exhibited in Figure 2 for a thermoplastic compound where different resistivity–temperature curves are obtained for different runs, namely, the thermoplastic compound has a poor electrical reproducibility.   Attempts to overcome this problem were made by adding rubber as a "mechanical stabilizer" to carbon black/wax mixtures[1] and by using mixtures of two carbon blacks with polyethylene.[5] Although significant improvements of the reproducibility were achieved, these were insufficient for practical applications.   The present solution, namely, crosslinking as structural stabilizer, functions satisfactorily as shown in Figure 2.   Only the first run is different from the subsequent
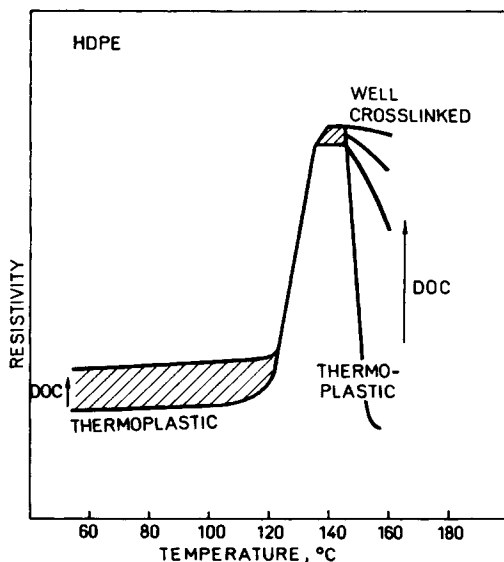

Fig. 1. Schematic representation of resistivity–temperature curves of polyethylene/conductive carbon black samples for various degrees of crosslinking (DOC).
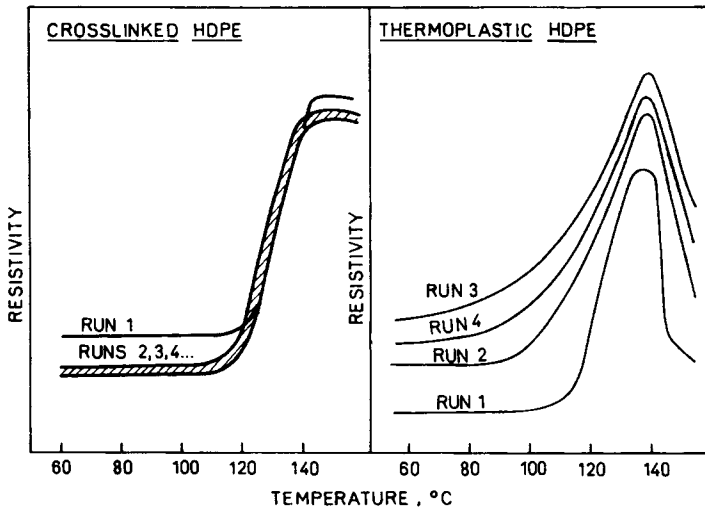
Fig. 2. Reproducibility of resistivity–temperature curves upon repeated temperature cycling.
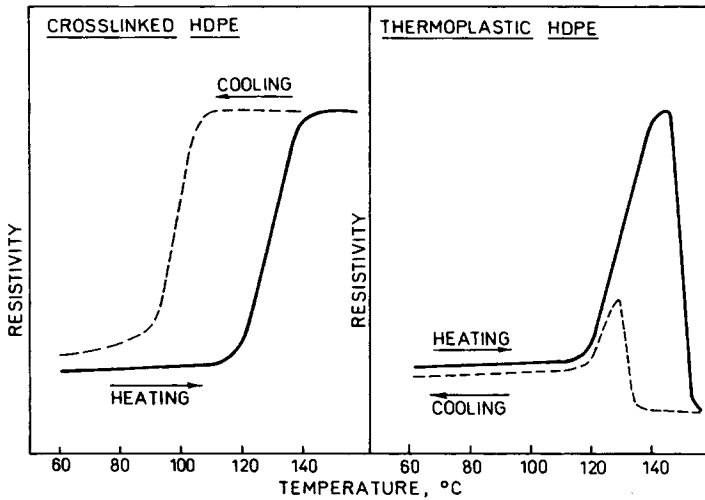

Fig. 3. Resistivity–temperature curves upon heating and cooling.

ones, and the resistivity–temperature curve for the well-crosslinked sample is characterized by very good reproducibility and the absence of the NTC phenomenon. In most reproducibility experiments the resistivity–temperature curves shifted downward relative to the first run for the crosslinked samples, while an upward shift was initially found in many thermoplastic samples followed by unpredictable trends.

A tremendous difference between crosslinked samples and their thermoplastic counterparts is found by comparing resistivity–temperature curves of complete heating/cooling cycles as shown schematically in Figure 3. The main difference stems from the fact that the crosslinked sample has no NTC effect and therefore its cooling curve is merely an approximate shift of the heating curve along the temperature axis.

In summary, carbon black-loaded thermoplastic polyethylene compounds are shown to be of little concern for practical uses, whereas crosslinking of these compounds yields products of satisfactory performance and of great potential for practical applications. A detailed description of the electrical behavior of crosslinked compounds containing varying concentrations of different carbon blacks will be given in a future article.

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M. NARKIS
A. RAM
Z. STEIN

Department of Chemical Engineering
Technion-Israel Institute of Technology
Haifa, Israel