Polyethylene/Carbon Black Switching Materials

Increasing amounts of an electrically conductive filler introduced into a polymeric matrix will show a sharp decrease of the electrical resistivity at a critical filler content and a common temperature. Observation of resistivity–temperature curves of crystalline polymer/conductive filler systems characterized by the critical filler content, or slightly higher, shows a sudden resistivity increase in the polymer melting region.[1,2] The resistivity change is an effect of several orders of magnitude giving materials with switching properties. The sharp volume expansion characteristic to the melting region results in volumetric content reduction of the conductive filler. This effect is considered as one of the reasons accounting for the sudden resistivity increase described by a positive temperature coefficient (PTC). Typical conductive fillers are carbon blacks, carbon filters, and metallic powders (silver, copper, nickel, etc.).

Three main types of carbon black are being used in conjunction with rubbers and plastics: channel blacks, furnace blacks, and thermal blacks. These carbon blacks vary widely in physical and chemical properties. Physically, they vary in particle size, aggregate shape or structure, and porosity; while chemically, they vary in regard to the oxygenated structures combined with their surface.

Bueche[2] used hydrocarbon wax/carbon black (type HAF) systems at a black content of about 7% by volume. Meyer[3] used polyethylene/carbon black (furnace black, Vulcan V3, Cabot Corp) systems comprising about 20% black by volume. The purpose of the present communication is to show that

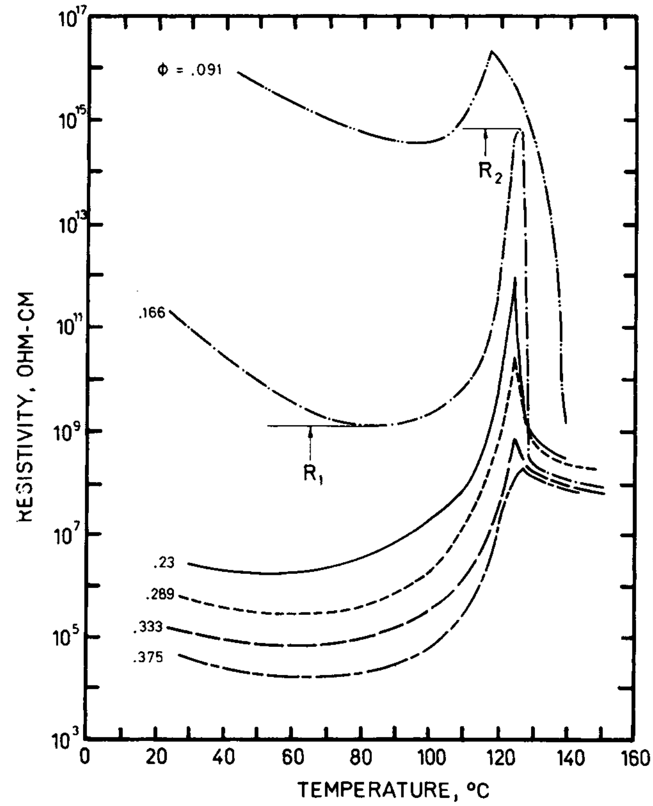

Fig. 1. Resistivity–temperature curves for various contents of MT black (curves represent the first run on the samples) in high-density polyethylene.

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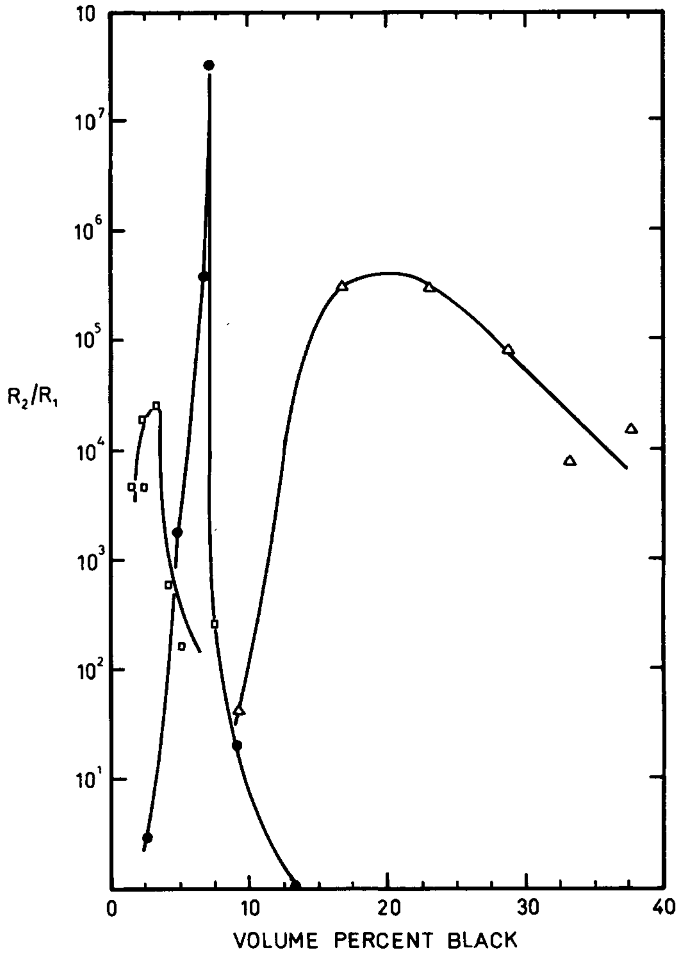

Fig. 2. Intensity of PTC (R_2/R_1) vs carbon black loading for different types of carbon black: (□) Ketjenblack EC; (●) ISAF; (△) MT black.

optimum PTC values with different grades of carbon black are achieved by using different contents of black, each content representing a specific carbon black. In general, it is agreed that enhanced conductivity in carbon blacks is a result of smaller particle size, higher structure, and higher porosity. Surface chemistry, although of secondary importance, results in less conductivity due to the presence of chemisorbed oxygen groups. For this reason, channel blacks are usually not used to impart conductivity to plastics.[4]

In the present work, three types of carbon black were used: Ketjenblack EC (furnace black, Akzo Chemie, Netherland), ISAF (furnace black, Israel Petrochemical Enterprises), and MT black (medium thermal black, Vanderbilt). Some properties of these carbon blacks are summarized in Table I, showing that Ketjenblack and ISAF (furnace blacks) have similar particle sizes. However, Ketjenblack has a very high effective surface area due to the contribution of internal voids. Ketjenblack EC is also characterized by very high electrical conductivity. Samples of carbon black and powdery high-density polyethylene (Sclair 8507G, du Pont Canada, MFI = 7 g/10 min) were dry blended, roll milled, and compression molded. Resistivity measurements were taken with the Keithly solid-state electrometer, Model 610-C.

Typical resistivity–temperature curves for different contents of the MT black are shown in Figure 1 for the first run of the samples. The problem of reproducibility[5] will be discussed in a detailed future article, while here, it is only pointed out that significantly improved reproducibilities can be

TABLE I
Typical Properties of Carbon Blacks Used in the Present Work

Properties	Ketjenblack EC Furnace black	ISAF Furnace black	MT Thermal black
Surface area BET (N_2), m^2/g	1000	120	6
Particle size, Å	300	220	5000
Pore volume (DBP), ml/100 g	340	125	33
Volatiles, %	1.0	2.0	0.5
pH	9.5	7	8

achieved by mixing different types of carbon black (varying in particle size), thus apparently causing a better packing. Figure 1 shows clearly the PTC effect as well as the descending room-temperature resistivity values by increasing the carbon black content. The PTC intensity for a certain carbon black content is determined by the resistivity ratio R_2/R_1, as shown in Figure 1 for a black volume fraction of 0.166.

PTC intensities for the three carbon blacks are shown in Figure 2 as a function of the black volume fraction. Figure 2 consists of three different curves located in a logical order and showing optimal contents as follows: Ketjenblack, 3.2%; ISAF, 7.0%; and MT black, 20% by volume. Current flow through a conductive plastic must take place via the conductive particles since the polymer is an insulator. For electrons to flow, the carbon black aggregates must be in contact or separated by very small distances. A distance of less than 100 Å is considered to permit electron flow through the polymer barrier.[6,7] Therefore, distance reduction between particles or aggregates increases conductivity, in agreement with the present results. Roughly speaking, one can conclude from Figure 2 that carbon blacks with better conductivity will give optimum PTC at lower concentrations. In addition, the more conductive carbon blacks are represented by narrower peaks, leading to increased sensitivity toward fluctuations in concentration around the optimum content. No conclusions can be made regarding the peak height. Finally, Figure 2 is very useful, as mentioned earlier, for designing optimum carbon black mixtures which are one step further toward practical applications where reliability and reproducibility are an inevitable necessity.

References

1. F. Bueche, *J. Appl. Phys.*, **43,** 4837 (1972).
2. F. Bueche, *J. Appl. Phys.*, **44,** 532 (1973).
3. J. Meyer, *Polym. Eng. Sci.*, **13,** 462 (1973).
4. J. H. Smuckler and P. M. Finnesty, *Performance of Conductive Carbon Blacks in a Typical Plastics System,* Technical Service Report S-24, Cabot Corp.
5. J. Meyer, *Polym. Eng. Sci.*, **14,** 706 (1974).
6. M. H. Polley and S. T. Boonstra, *Rubber Chem. Technol.*, **30,** 170 (1957).
7. A. Voet, *Electrical Conductance of Carbon Black,* 12th Annual Wire and Cable Symposium, Asbury Park, N.J., 1963.

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