Resistivity Behavior of Filled Electrically Conductive Crosslinked Polyethylene

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Synopsis

The electrical resistivity of crosslinked high-density polyethylene loaded with conductive blacks and carbon fibers was studied as a function of filler concentration and temperature. A thermoelectric switching phenomenon (a sudden resistivity increase in the vicinity of the polyethylene melting point) in such semicrystalline conductive systems was investigated. Significant switching properties were found only in compounds useful in the medium conductivity range. A significant switching behavior was exhibited by compounds containing very low concentrations of carbon fibers. Some crosslinked compounds filled with mixtures of carbon black and carbon fibers were also studied.

INTRODUCTION

Electrically conductive plastics are becoming nowadays increasingly important. Application fields include antistatic products, self-heating plastics, shielding materials (RFI and EMI), and electromagnetic radiation absorbing materials. Some conductive compounds also exhibit a thermoelectric switching behavior where in the vicinity of the polymer transition region the compound shows a dramatic resistivity increase which can be utilized for self-regulation purposes. Compounds suitable for these various applications differ appreciably in the nature of their components and their composition, depending on the specific performance required. A variety of conductive fillers is presently being offered to material engineers, including carbon blacks, carbon fibers, metallic powders, flakes or fibers, and glass spheres or glass fibers coated with metals.[1,2] A summary of the technology and physics of electrically conducting elastomers and plastics containing carbon blacks and carbon fibers can be found in the some recent books.[3-7]

This paper describes crosslinked polyethylene systems containing carbon blacks and carbon fibers in relation to the behavior of their electrical resistivity. The introduction of crosslinks into thermoplastic polyethylene is vital in order to preserve the good mechanical properties of the filled polymer and to impart good electrical reproductibility behavior during heating–cooling cycles.

EXPERIMENTAL

Compounds of polyethylene, carbon black, or carbon fibers, and peroxide were compression-molded at 190–200°C giving about 3 mm thick plaques. Radiation crosslinking was done by irradiating thermoplastic plaques with a Co^{60} source

TABLE I
Properties of Electrically Conductive Carbon Blacks

Properties	Ketjen EC	XC-72	Corax L6	Conductex 975	Conductex 40-220
Surface area N_2 BET (m^2/g)	1000	180	265	250	1050
Particle size (Å)	300	290	180	220	160
Pore volume DBP $(mL/100 g)$	350	178	123	165	260
EM surface area (m^2/g)	108	111	135	130	185
CTAB (m^2/g)	480	86	150	153	515
Pore area (m^2/g)	449	94[a]	115	97[a]	535[a]
Iodine absorption (mg/g)	900	—	293	260	1035
Volatiles (%)	0.5	1.0	1.5	1.0	1.6
pH	8	7	7.5	7	6

[a] Pore area estimated by subtraction of CTAB from N_2 surface area.

in vacuum using a dose of 25 Mrad. The degree of crosslinking was determined by a gel test in boiling xylene. Crosslinking procedures, gel testing, and resistivity measurements were described in previous publications.[8,9] Resistivity measurements were done after placing aluminum foils on the surfaces of the samples.
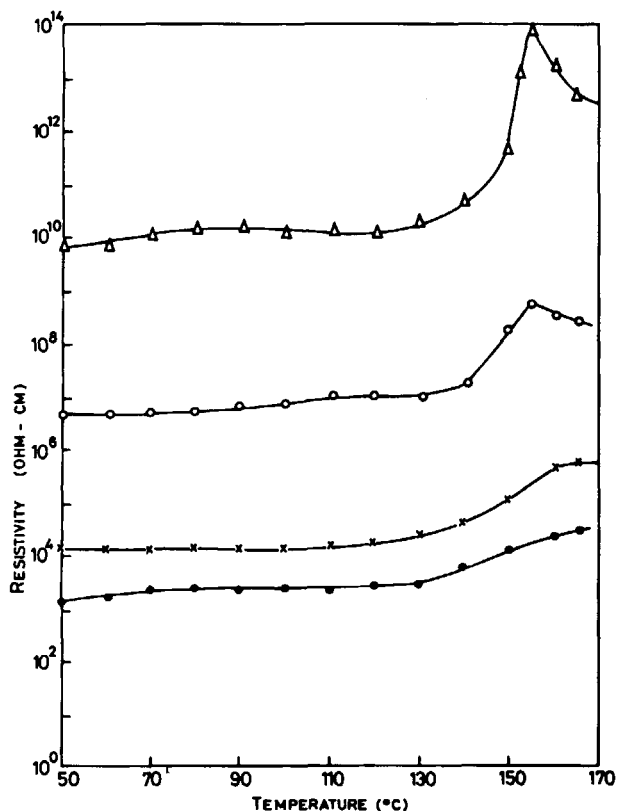

Fig. 1. Resistivity-temperature curves of peroxide crosslinked polyethylene containing XC-72 black (% w/w): (●) 20; (×) 15; (○) 10; (△) 5.
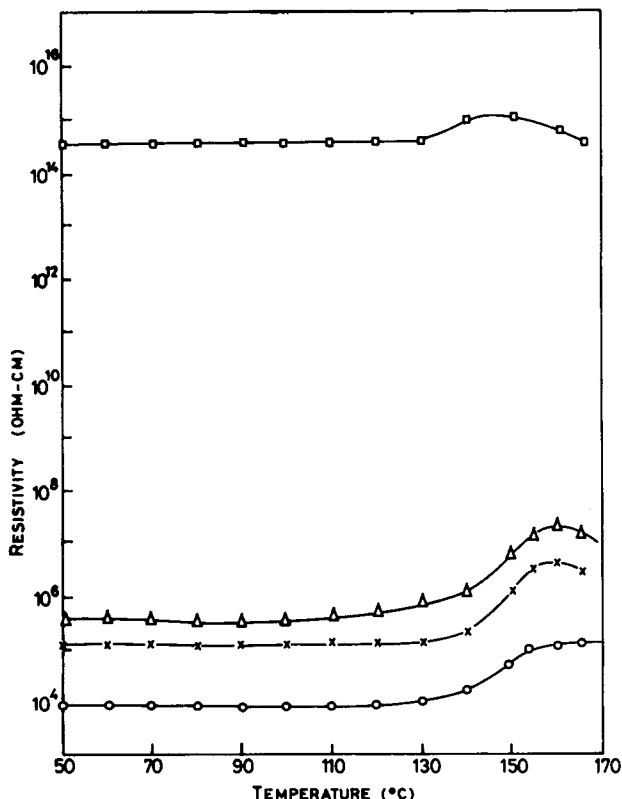
Fig. 2. Resistivity-temperature curves of peroxide crosslinked polyethylene containing Corax L6 black (% w/w): (O) 20; (X) 15; (△) 10; (□) 7.

Resistivity measurements reported in this paper represent values taken in a second heating–cooling cycle.

The polyethylene used in this work had a density of 0.95 g/cm^3 and a melt flow index of 4 g/10 min. The following carbon blacks were used: Ketjenblack EC (Akzo Chemie, The Netherlands), XC-72 (Cabot), Corax L6 (Degussa, West Germany), and Conductex 975 and Conductex 40-220 (Columbian Chemical). A summary of typical properties of these carbon blacks is given in Table I. The short carbon fibers used had a length of 6 mm (Grafil A-S, Courtaulds, United Kingdom).

RESULTS AND DISCUSSION

Electrically conductive carbon blacks consist of very fine particles (100–500 Å) fused together to form an aggregate. The number of particles per aggregate and aggregate shape both affect the conduction level of aggregate/polymer composite systems. "High-structure" carbon blacks contain aggregates having large numbers of particles per aggregate. High structure and elongated aggregates are in favor of better conductivity levels. The structure or aggregate morphology of carbon blacks is measured by adding dibutyl phthalate (DBP)
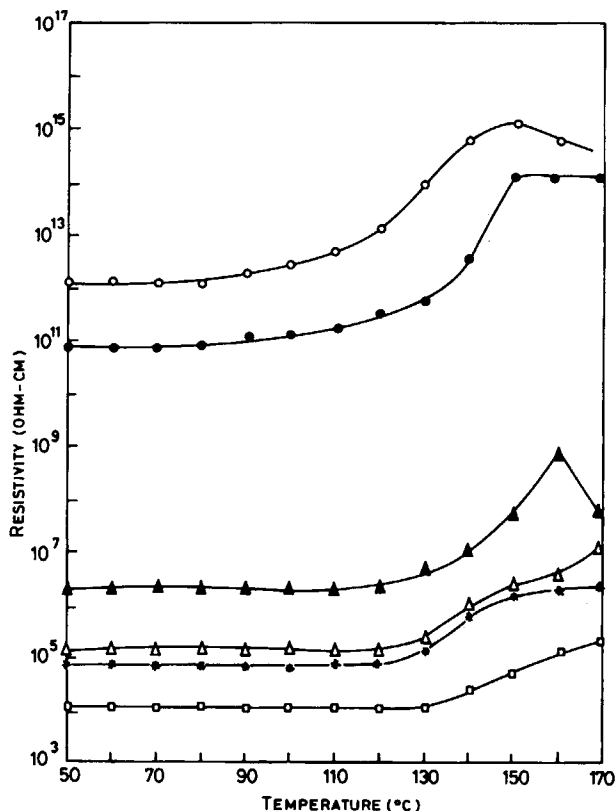
Fig. 3. Resistivity-temperature curves of peroxide crosslinked polyethylene containing Conductex 975-black (% w/w):   (O) 5; (●) 6; (▲) 7; (△) 10; (✳) 15; (□) 20.

to fill the void spaces within and between particles.   In addition to high structure and anisometric shapes, high microporosity (particle pores smaller than 20 Å in diameter or width) is also important in enhancing the electrical conductivity. Microporosity can roughly and indirectly be deduced from surface area measurements by nitrogen adsorption (capable to detect micropores) and CTAB (cetyltrimethylammonium bromide) adsorption (CTAB molecules are too big to penetrate into the micropores).   Thus nitrogen adsorption may reflect the external and internal (micropores) surfaces whereas CTAB adsorption represents the external surface only.   Microporosity values expressed as "pore area" in Table I are obtained by subtraction of the CTAB surface area from the nitrogen surface area.   In practice, carbon blacks have to perform after their incorporation into elastomer and polymer matrices.   During the compounding-fabrication step breakdown of aggregates and agglomeration–deagglomeration processes of particles and aggregates may take place, affecting the electrical performance and reproductibility of the conductive products.   High-structure blacks are naturally especially prone to breakdown.   Agglomeration–deagglomeration processes may also occur by mechanical deformations and by thermal expansion and contraction processes.

Figures 1–4 show the resistivity–temperature behavior at various carbon black
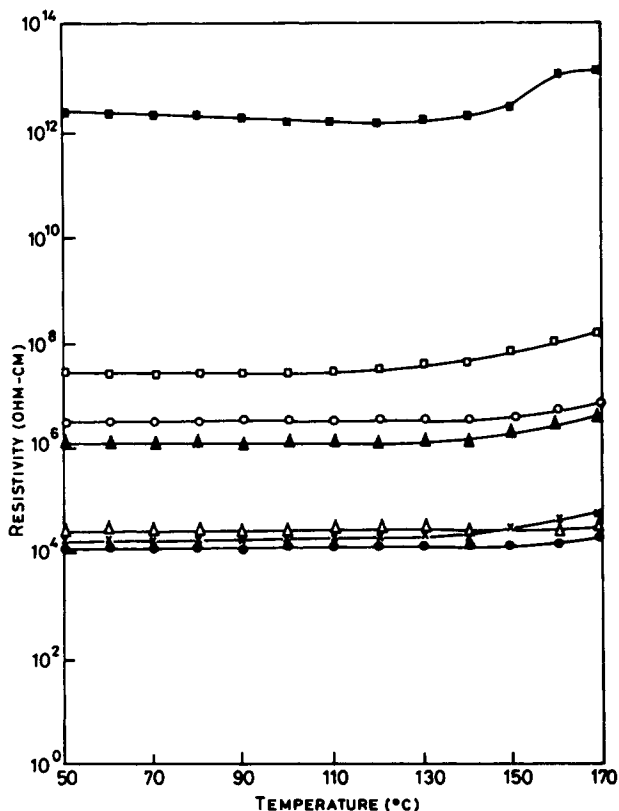
Fig. 4. Resistivity-temperature curves of peroxide crosslinked polyethylene containing Conductex 40-220 black (% w/w): (●) 20; (X) 15; (△) 12; (▲) 10; (○) 8; (□) 5; (■) 3, 5.

concentrations of composites containing the carbon blacks shown in Table I (similar data for EC black composites were reported previously[9]). The room temperature resistivity as function of the black concentration for carbon blacks given in Table I is shown in Figure 5. Inspection of Table I and additional information supplied by the carbon black producers reveals that EC black is owing its superior conductivity to a very high microporosity value. Electron microscopy investigations of EC black aggregates classify their morphology as low-structure aggregates. Thus, repeated crushing of dry EC black has caused only a slight reduction in the DBP value and the sensitivity of composites containing EC black processing history was also small.[10] XC-72 black is a high-structure, somewhat porous material characterized by highly extended aggregates and by an exceptionally broad particle and aggregate size distribution assisting in the formation of a strong network, all contributing to enhanced conductivities. Corax L6 is a relative new furnace black recommended for production of antistatic or conductive rubber and plastic compounds. Corax L6 is an improved version of Corax L characterized by an increased surface area and high structure. Conductex 975 is a furnace black of medium porosity, highly elongated domains (high structure), and broad particle size distribution. Conductex 40-220 consists of very small particles which are virtually hollow and have a very high surface area.
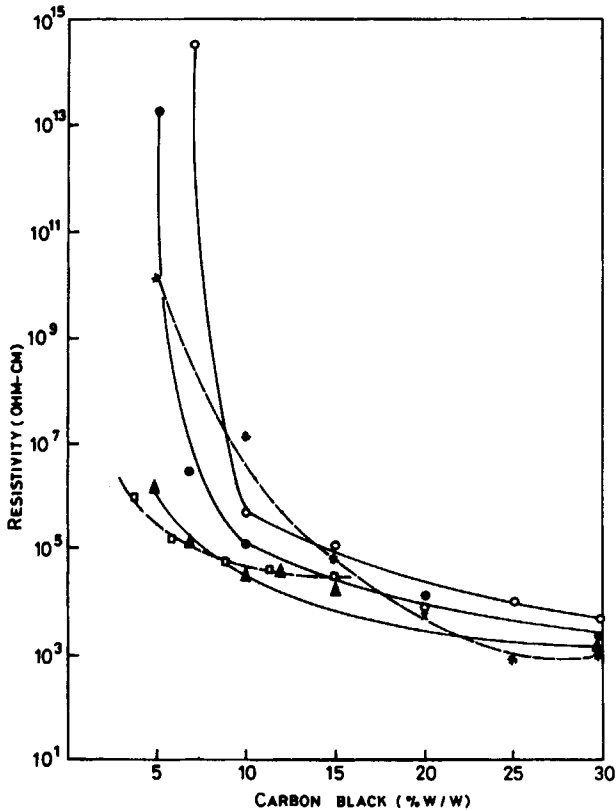
Fig. 5. Room temperature resistivity ρ_{RT} as function of carbon black concentration in peroxide crosslinked polyethylene for different carbon blacks: (●) Conductex 975; (○) Corax L6; (∗) XC-72; (▲) Conductex 40-220; (□), EC.

This carbon black is highly structured and has a relatively low volatile content (high purity). Ketjenblack EC and Conductex 40-220 are the most conductive carbon blacks presently known. XC-72, Corax L6, and Conductex 975 represent conductive carbon blacks useful in the medium conductivity range.

Electron conduction in carbon-black-filled polymers occurs along particles contacting each other or separated by very small gaps. These interaggregate gaps may be considered as potential barriers for electrons to hop by tunneling. Reduction of the interaggregate gaps enhances the flow of electrons and decreases the macroscopic resistivity. The average interaggregate distance is affected by many parameters including concentration, structure, size and shape of the aggregates, size distribution, mixing efficiency, temperature, etc. Conductor–insulator composites become conductive only after a certain threshold concentration of the conductive filler has been added. This critical percolation threshold represents a system where continuous conductive chains have been first formed. The conducting elements of these chains are either making contacts between themselves or separated by very small distances across which electrons can hop by tunneling. The experimental volumetric percolation concentrations representing good electrically conductive carbon blacks are usually far below theoretical predictions or experimental data for spherical conducting elements
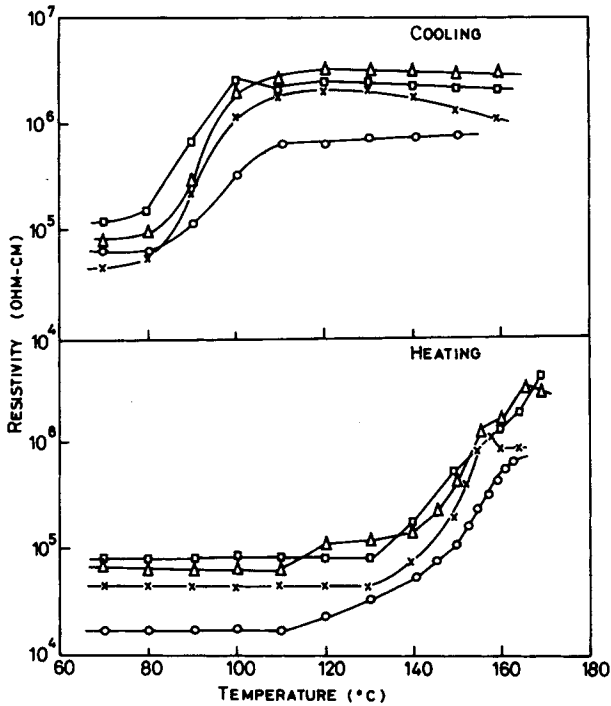
Fig. 6. Resistivity-temperature curves upon heating and cooling of peroxide crosslinked polyethylene sample containing 0.15 w/w XC-72 black. Run nos.: (O) 1; (X) 2; (△) 3; (□) 4.

(metal powders, for example) dispersed in polymers. The main reason for this "discrepancy" is attributed to the unique aggregate structure, rather than individual spherical particles, of carbon blacks. This aggregate structure leads to a filamentary conducting network requiring significantly lower concentrations to reach the critical percolation concentration. Thus, the threshold concentration is roughly attained by adding 25% v/v individual metal spheres, 5% v/v conductive carbon blocks, or 1% v/v high aspect ratio metal or carbon fibers. The nature of the host polymer matrix is also important regarding the critical percolation concentration of the conductive filler. Thus, in semicrystalline polymers the very fine carbon black aggregates tend to concentrate in amorphous regions. During the crystallization process a major part of the carbon black aggregates is rejected into interspherulitic boundaries and the rest may be located in amorphous regions within the spherulites. As a result, the threshold percolation concentration in semicrystalline systems is lower than in amorphous polymers. Critical concentrations for the carbon blacks studied in this work can be deduced from Figure 5. If a resistivity of 10^8 $\Omega \cdot$ cm is chosen to represent the insulator–conductor transition then all the characteristic critical concentrations fall below 10% w/w or about 5% v/v of the dispersed carbon black. Although the general trends of the resistivity–concentration curves shown in Figure 5 are similar, the curves themselves sometimes overlap and intersect. The exact shape of these curves depends on too many factors to be accounted for theoretically, and their detailed prediction possibility seems far remote, at the present time.
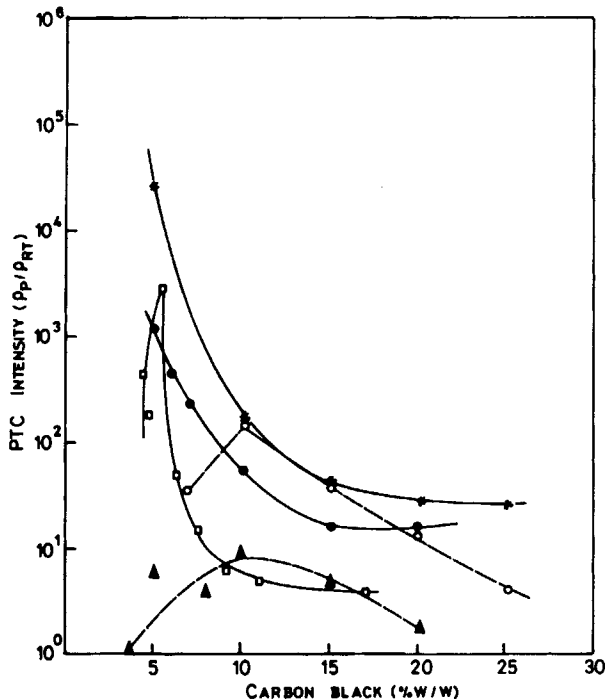
Fig. 7. PTC intensity (ρ_{peak}/ρ_{RT}) as function of carbon black concentration for different carbon blacks: (●) Conductex 975; (∗) XC-72; (O) Corax L6; (▲) Conductex 40-220; (□) EC.

As previously discussed, conductor-filled systems are becoming conductive only after a certain critical threshold concentration of the conductive filler has been added. Such systems consisting of the critical concentration become insulative if their interaggregate distances increase by external means such as thermal expansion or mechanical stressing. Conductor-filled semicrystalline systems show a sharp resistivity increase in the vicinity of the polymer melting point (PTC = positive temperature coefficient of resistivity[11-17]). This resistivity increase is often followed by a rapid resistivity decrease (NTC = negative temperature coefficient of resistivity). Compounds showing the PTC effect have a thermoelectric switching behavior which may be utilized in practice. In this regard the NTC phenomenon is a serious drawback since the switching properties imparted to a system by the PTC effect may lose their significance once followed by a distinguished NTC behavior. The NTC effect can be eliminated in practice by peroxide or irradiation crosslinking of carbon-black-loaded polyethylene.[9] The absence of the NTC effect is shown in Figure 6, where the cooling curves start at high resistivities similar to the peak resistivities obtained upon heating. This figure also shows that the electrical reproducibility improves by thermal cycling.[9] Although the NTC phenomenon is not well understood, from its absence in the crosslinked compounds, one can conjecture that it is associated with the significant reduction in movement opportunities of the particles tightly held in, or linked to, a crosslinked rubbery (rather than fluid) network.

In the cable industry where semiconductive compounds are required the presence of a PTC effect is undesired and should be accounted for in cable design.
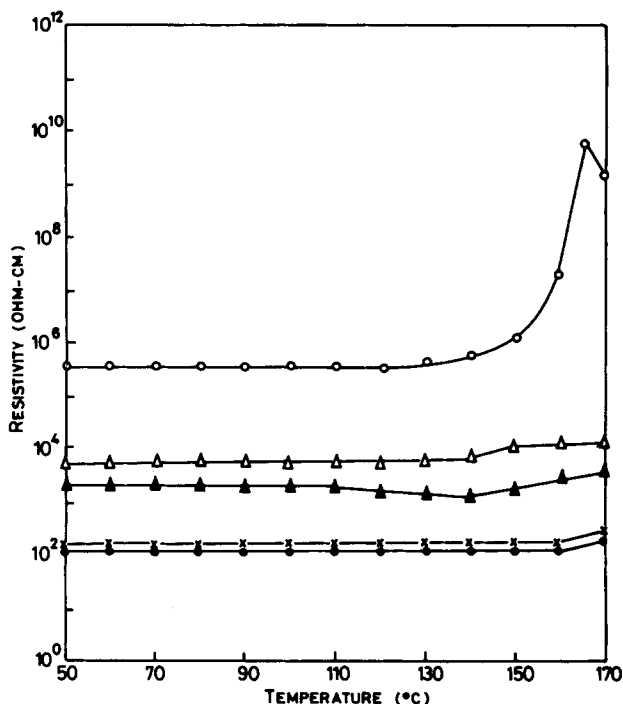
Fig. 8. Resistivity-temperature curves of peroxide crosslinked polyethylene containing carbon fibers. Mixing procedure of polyethylene and carbon fibers by dry-blending. % w/w carbon fibers: (●) 20; (X) 15; (▲) 10; (△) 5; (O) 2.

In this industry, however, the semiconductive compounds employed often are characterized by PTC intensities relatively small compared to the maximum PTC intensities obtained in compounds roughly containing the threshold percolation concentration. For switching purposes, if a high conductivity is required, highly filled compounds should be employed. Such highly conductive compounds, however, very seldom show good switching behavior; thus compounds combining high conductivities and significant switching properties are still a curiosity. Figure 7 shows that carbon black concentrations giving the maximum PTC intensity lie between 5% and 10% w/w, a loading level giving only moderate conductivities.

In the past 3 years a significant progress has been made related to better characterization, correlation, control, and understanding the PTC phenomenon.[9,16,17] These recent studies dealt with relationships between carbon black parameters and PTC intensity, crosslinking effects, and theoretical analyses of the effects of some distinct physical processes on electron transport in PTC materials.

The electrical conductivity of carbon and graphite fibers has been of interest to many industries and numerous applications have been devised.[7] Carbon and graphite fibers are carbonized materials by pyrolysis and graphitized by heat treatment. Acrylonitrile fibers and petroleum pitch formulations serve as precursor materials, undergoing the pyrolysis and graphitization processes yielding electrically conductive high-strength, high-modulus fibers. These fibers show
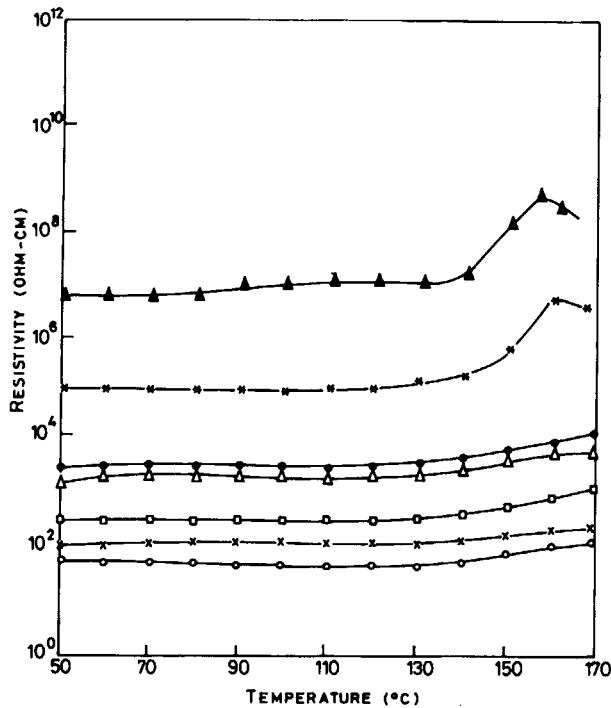
Fig. 9. Resistivity-temperature curves of peroxide crosslinked polyethylene containing 0.10 w/w XC-72 black and various concentrations of carbon fibers. Mixing procedure of polyethylene with XC-72 by hot roll-milling and grinding to small particles followed by dry-blending of the XC-72 containing particles with carbon fibers (% w/w): (▲) 0; (✻) 1; (●) 2; (△) 5; (□) 10; (×) 15; (○) 20.

higher electrical conductivities for increasing graphite contents. Their performance in polymer composites is highly dependent upon the fiber aspect ratio; thus fiber attrition during compounding and fabrication should be minimal. Compounding procedures of carbon fibers with thermoplastic matrices have recently been summarized.[7]

In the present work preparation methods included cold dry-blending or hot roll-milling followed by compression molding. Crosslinking methods of the carbon fiber/polyethylene composites consisted of peroxide crosslinking during the compression molding operation or irradiation crosslinking in vacuum of compressed sheets. Little fiber breakage occurred during the dry-blending operation; however, satisfactory uniformity of fiber dispersion could not be achieved by dry-blending. Figure 8 shows that already at 2% w/w, an extremely low fiber content, an impressive conductivity coupled with a very pronounced PTC intensity are obtained, while at 5% w/w fibers the PTC intensity is very small. Thus only at very low fiber concentrations fiber contacting and overlapping are broken during the system's expansion step accompanying the melting process. Fiber overlapping and contacts are essentially retained in compounds containing 5% w/w or more fibers resulting the insignificant PTC intensities. Here again a combination of high conductivities and significant switching levels cannot be achieved. Upon the addition of a constant carbon black concentration to the fiber/polyethylene compounds significant resistivity reductions are ob-
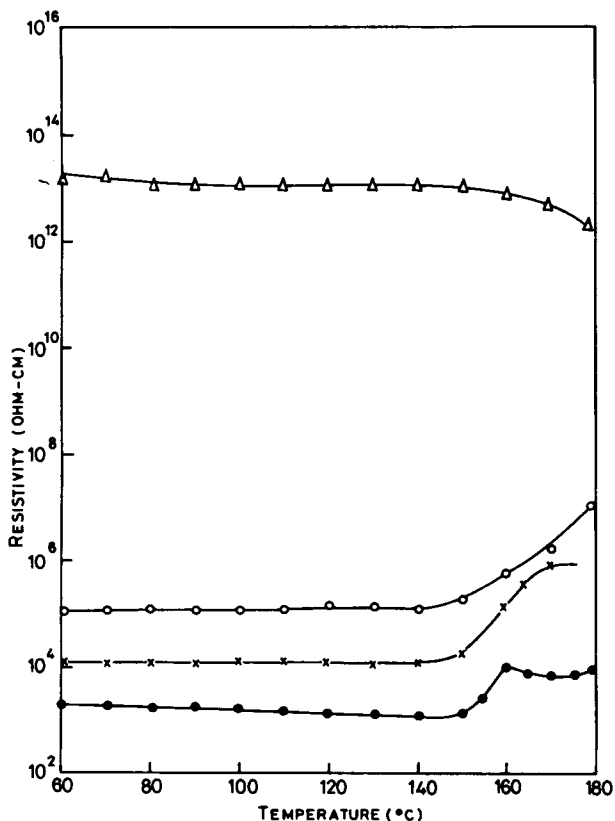
Fig. 10. Resistivity-temperature curves of irradiation crosslinked polyethylene containing carbon fibers. Mixing procedure of polyethylene and carbon fibers by hot roll-milling; (% w/w): (●) 20; (×) 10; (○) 5; (△) 2.

tained; however, high conductivities coupled with significant switching properties are not achieved, as shown in Figure 9. It seems that high PTC intensities may be feasible in conductive carbon fiber/carbon black/polyethylene systems at very low fiber concentrations (less than 1% w/w). Such three-component composites have not been produced in the present work due to experimental difficulties related to a uniform dispersion of the fibers at such low concentrations. Samples prepared by hot roll-milling, compression molding, and crosslinking by irradiation are shown in Figure 10. At 2% w/w a nonconductive sample is obtained (compare with Fig. 8) due to fiber attrition during the roll-milling step. At the higher fiber concentrations the composites have significant PTC intensities (compare with Fig. 8) due to the reduction of the fiber aspect ratio, resulting in less overlapping and less permanent conducting paths. The lower curve in Figure 11 represents a three-component system containing 2% w/w fibers added by dry blending. An identical composition represents the middle curve in this figure; however, fibers have been added by hot roll-milling. The resistivity increase and very pronounced PTC intensity obtained demonstrate how fiber breakage in similar compounds may affect the electrical performance. For comparison,
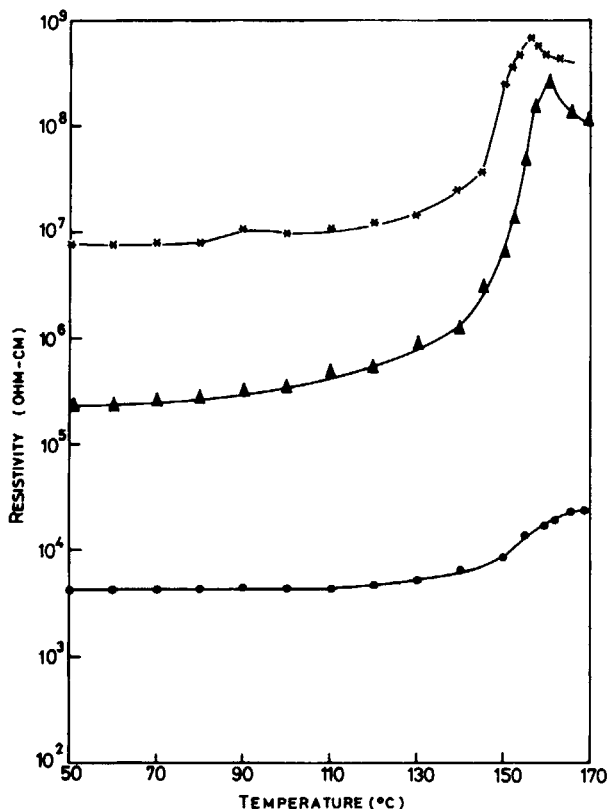
Fig. 11. Resistivity-temperature curves of peroxide crosslinked polyethylene containing 0.10 w/w XC-72 black and (●) 0.02 w/w carbon fibers added by dry-blending, (▲) 0.02 w/w carbon fibers added by hot roll-milling, (✱) no fibers.

the upper curve shown in Figure 11 represents a fiber-free sample containing the same ratio of carbon black/polyethylene components as in the two other samples shown in the figure. Figure 11 also shows that by a very careful selection of three-component systems and sometimes with some intentional fiber attrition (or starting with shorter fibers) compounds having desired unique properties can be produced. Figures 12 and 13 were derived from the data given in the previous figures. These two figures show the variation of room-temperature resistivity and PTC intensity with carbon fiber concentration in polyethylene and in carbon black/polyethylene mixtures (fibers added by dry-blending).

In a future paper the mechanical properties of high-density peroxide and irradiation crosslinked polyethylene filled with carbon blacks and carbon fibers will be described.
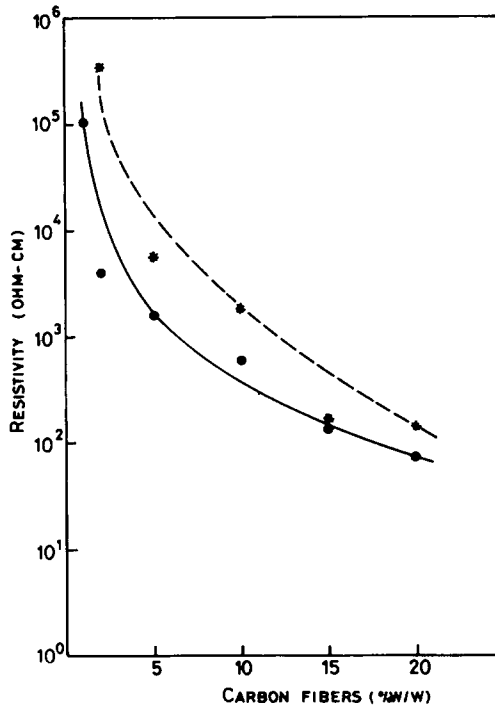
Fig. 12. Room-temperature resistivity ρ_{RT} as function of carbon fiber concentration in peroxide crosslinked polyethylene. (●) Samples contain also 0.10% w/w XC-72 carbon black, (✶) fibers only. Carbon fibers added by dry-blending.
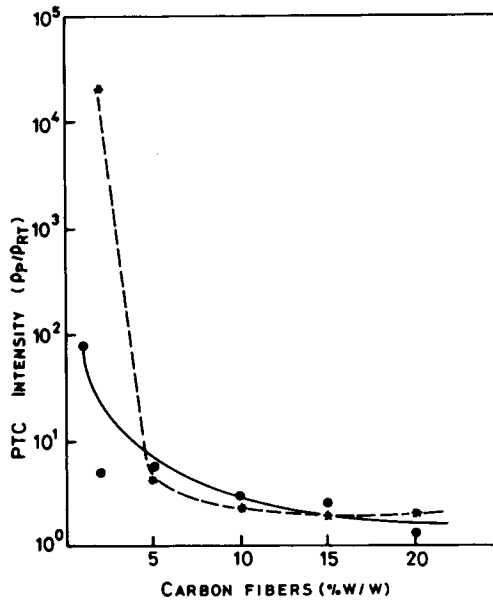

Fig. 13. PTC intensity (ρ_{peak}/ρ_{RT}) as function of carbon fiber concentration. (●) Samples contain also 0.10% w/w XC-72 carbon black, (✶) fibers only. Carbon fibers added by dry-blending.

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