# A new class of switching materials

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By combining several volume percent of conducting particles in a semicrystalline matrix, a highly temperature-dependent resistivity is obtained. The resistivity changes by several orders of magnitude in a small temperature interval centered on the crystal melting temperature. Moreover, a typical resistivity changes by a factor of hundreds as the frequency changes from $10^2$ to $10^4$ Hz. Materials of this type show dielectric constants in excess of $10^3$ which vary strongly with temperature and frequency.

When a particulate electrical conducting filler is added to a nonconducting matrix, the system undergoes a sharp transition from nonconductor to conductor at a critical volume percent of filler, typically about 7%.[1,2] We point out here how this effect can be used to produce materials with switching possibilities. Although many systems can be envisaged, we shall describe only some of the simplest at this time.

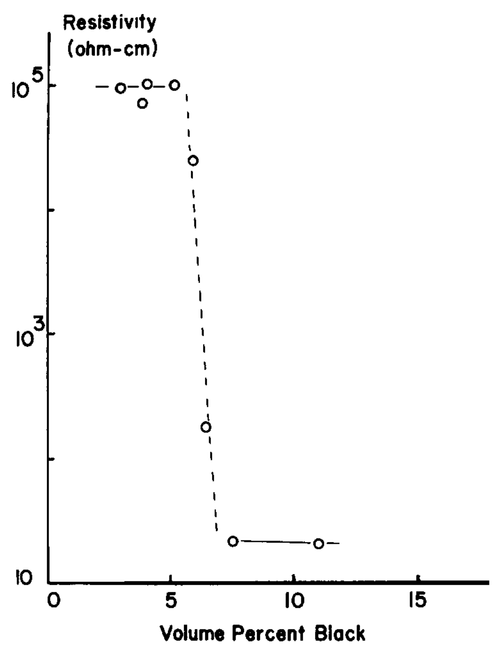

FIG. 1. The variation of electrical resistivity with volume percent black for a carbon black-$C_{36}H_{74}$ system.

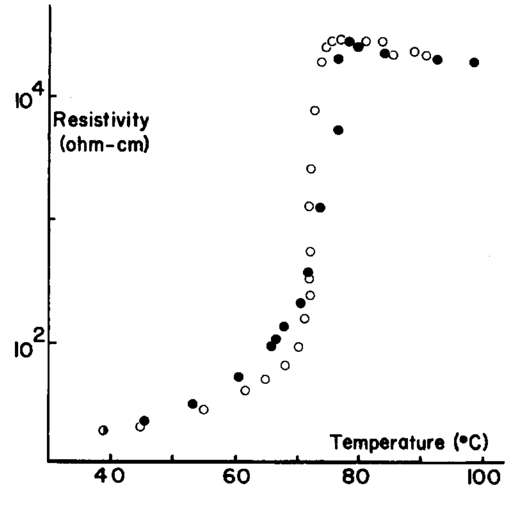

FIG. 2. The temperature dependence of electrical resistivity for a carbon black-$C_{36}H_{74}$ system containing 7.6 vol % black. Filled circles indicate ascending temperatures.

Shown in Fig. 1 is the room-temperature electrical resistivity of carbon black (type HAF) dispersed in a hydrocarbon wax, $C_{36}H_{74}$. (Dispersal was effected by dissolving the molten wax in heptane and subjecting the mixture to ultrasonic vibration with subsequent drying). Note that the resistivity drops precipitously at about 6 vol % carbon black. This is in the region where theory predicts such a change.[2] Some uncertainty exists in the concentrations shown in Fig. 1 since the effective density of the black is uncertain (we use 2.0 g/cm$^3$). In addition, the wax tended to bleed slightly.

Since the wax melts at 73 °C with a consequent increase of volume of about 22%, the volume fraction of black suddenly decreases as the temperature is raised above 73 °C. Choosing a room-temperature black concentration of 7.6% by volume, one observes the resistivity to change with temperature as shown in Fig. 2. As one would predict, the sudden change in volume at the melting point causes a sharp change in resistivity at that temperature. The two sets of points represent rising and lowering temperature sequences. These curves are repeatable and can be recycled. We see here an effect which can be used as a temperature-activated switch for electricity and presumably for heat

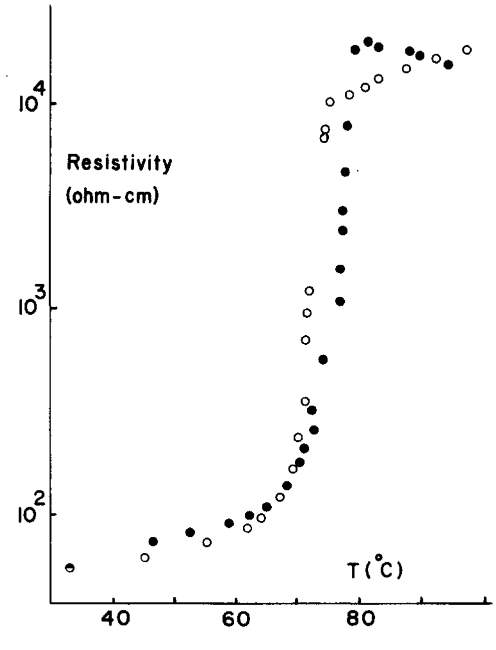

FIG. 3. Resistivity of a system containing the following volume percents of black, $C_{36}H_{74}$ and polyisobutylene, respectively: 0.11, 0.67, and 0.22.

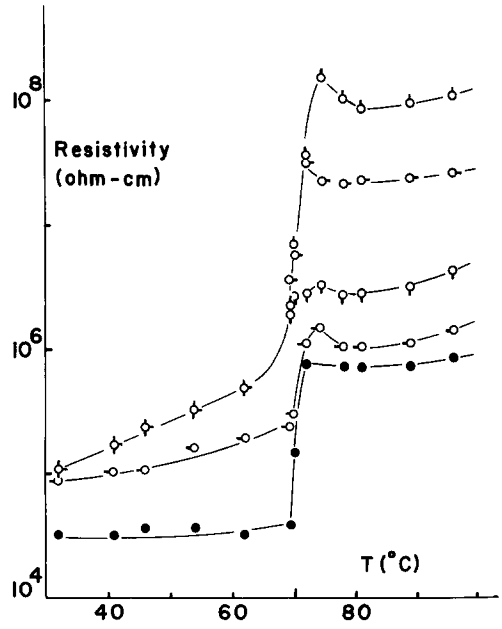

FIG. 4. Resistivity of a 0.077% black, 0.69% $C_{36}H_{74}$, and 0.23% polyisobutylene system at dc (ტ), $10^2$ Hz (O-), $10^3$ Hz (♀), $10^4$ Hz (-O) and $10^5$ Hz (●).

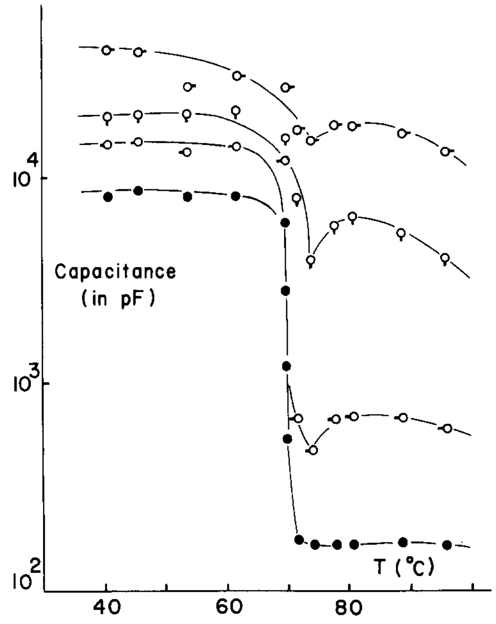

FIG. 6. Variation of capacitance for the material of Fig. 4. Frequency designations are the same as for Fig. 4.

also. Depending upon the cooling and heating rates, the material will exhibit memory of adjustable duration.

Another typical system is shown in Fig. 3. This material contains 0.22 vol % polyisobutylene as a mechanical stabilizer for the molten system. Similar results are found when the polyisobutylene is replaced by styrene-butadiene rubber. Some difficulty was experienced in the use of polymers in which the molten wax would not dissolve since excessive bleeding occurs.

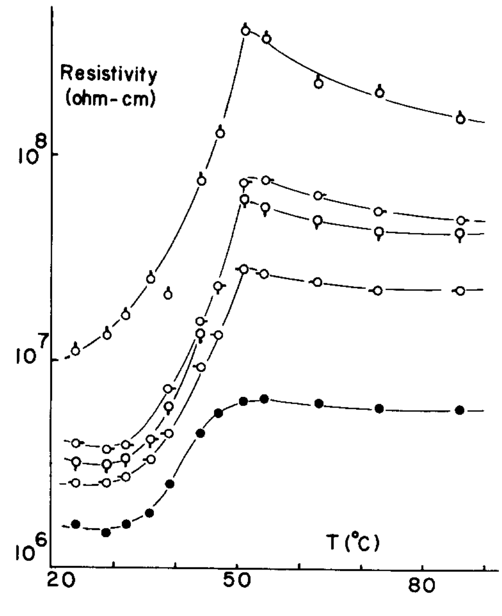

FIG. 5. Resistivity of a 0.080% black, 0.56% tetracosane, and 0.36% polyisobutylene system. See Fig. 4 for frequency designations.

When one examines the resistivity of these materials as a function of frequency, the behavior typified by Fig. 4 is found. Note that the resistivity shows a discontinuity at all frequencies but the absolute value varies markedly with frequency as well. Similar data on a different wax system (tetracosane, $C_{24}H_{50}$, melting point = 51 °C) are shown in Fig. 5. Here, too, the resistivity is highly frequency dependent but the transition is not nearly as sharp as for the other wax. We attribute this difference to the fact that the increased compatibility of this wax with the polymer component leads to a less distinct freezing-out temperature for the wax phase.

As one might predict, these systems should show anomalous dielectric behavior. When the material of Fig. 4 is sealed between flexible film aluminum electrodes (area 12.8 $cm^2$ and separation 0.150 cm), the capacitance varies as shown in Fig. 6. Since the air capacitance of the capacitor is only 7.5 pF, the material has an extremely high dielectric constant.

It is clear that the effects described here have analogues in many other systems. Any substance showing a sudden change in volume can be used in place of the wax. Hence the switching temperature can be varied widely and predictably. Carbon black is only one of many conductors which could be used. The frequency dependence is apparently related to the Wagner-type dispersion[3] found in two-phase materials. However, preliminary theoretical work indicates that the "phase" responsible is the relatively high-resistance agglomerates of the particles rather than the particles themselves.

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[1] S. M. Aharoni, J. Appl. Phys. 43, 2463 (1972).
[2] F. Bueche, J. Appl. Phys. 43, 4837 (1972).
[3] See C. P. Smyth, *Dielectric Behavior and Structure* (McGraw-Hill, New York, 1955), p. 73.