High T_c Superconductor Polymer Composite Based on $YBa_2Cu_3O_{7-x}$. II. Conduction Mechanisms and Temperature Effect on Conductive and Dielectric Properties of Polypropylene Composites

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SYNOPSIS

To improve the connectivity of YBaCuO particles in a polypropylene matrix, different amounts of carbon black (N) or copper (C) were incorporated into the binary base system. In this research the effects of these conductor fillers on the conduction mechanism of the experimental composites were studied using complex impedance spectroscopy as the analytical technique. In addition the effects of temperature on certain electrical properties were examined in the synthesized materials. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The inherent brittleness of most superconductor ceramics strongly conditions the technological development of these materials. Several solutions have been put forward to produce materials that would possess sufficient flexibility, mechanical strength, and good superconductor behavior, such as thin superconductor films deposited on various substrates,[1,2] superconductor/metal tapes,[3,4] and the incorporation of superconductor ceramic powders into polymers.[5,6] This research refers to the last of these solutions.

In previous work[7] the incorporation of superconductor ceramics of the type $YBa_2Cu_3O_{7-x}$ (Y) into polymeric polypropylene (PP) matrices was examined. This study highlighted the relevance of this synthetic approach from a practical point of view, and took into account that it does not only allow for conductor and superconductor property preservation of such ceramics, but also avoids early degradation in relatively conventional environments, significantly improving the mechanical properties of the end product and clearly favoring its processability. Thus with any conventional thermomolding method, any simple or complex profile or shape can be cast. Acosta et al.[7] examined the microstructure and electrical properties of superconductor PP and Y composites as well as the effects exerted by the presence of carbon black (N) or copper (C) on the properties of such composites.

In this work different composites obtained from blending PP, Y, and N or C were studied utilizing complex impedance spectroscopy to gain insight into the real behavior of such composites over a wide range of temperatures. For this purpose the study focused on two basic aspects: the study of the conduction mechanism and of the factors influencing it, and the determination of the conductor and electrical properties over a wide temperature range (70–400 K).

EXPERIMENTAL

The following raw materials were used in the experimental composites. High T_c superconductor powder Superamic Y 200 (<25 μm) was supplied by Rhône–Poulenc; carbon black Isaf (20–25 μm) was supplied by Cabot; and the copper filler (63 μm) was a Merck product.

The composites were prepared in a Brabender Plasticorder using a thermoplastic mixing chamber (60 W) preheated to 473 K. Rotor speed was set at

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Table I Electrical Properties of Samples

	Composition				Electrical Properties					
Samples	PP (Φ_v, %)	YBaCuO (Φ_v, %)	N (Φ_v, %)	Cu (Φ_v, %)	R (Ω)	C (F)	L (H)	σ (s cm^{-1})	n	Y_0 (mho)
PC-20	80			20	3.1E + 7	1.7E-10		4.7E-09		
PC-30	70			30	1.7E + 6	2.7E-10		2.4E-08		
PC-40	60			40	3.2E + 5	3.2E-10		1.9E-07		
PN-5	95		5		4.4E + 7	1.4E-10		4.1E-09		
PN-10	90		10		2.0E + 7	7.1E-10		2.8E-09		
PN-20	80		20		3.1		2.0E-06	0.0318		
PN-30	70		30		2.1		1.9E-06	0.0797		
PY-20	80	20			1.2E + 8	1.2E-09		1.2E-08		
PY-40	60	40			6.5E + 7			1.4E-08	0.91	1.0E-09
PY-55	45	55			1.6E + 7			1.3E-08	0.95	2.6E-10
PYC-1	50	40		10	1.0E + 7	2.8E-10		6.1E-09		
PYC-2	50	30		20	2.0E + 7	2.3E-10		4.5E-09		
PYC-3	50	20		30	4.5E + 5			2.8E-07	0.90	7.4E-10
PYC-4	50	10		40	1.4E + 5			1.4E-06	0.78	1.6E-09
PYN-1a	50	40	10		9.4E + 2			1.0E-4	0.53	9.7E-07
PYN-1b	50	40	10		7.9E + 2			1.0E-4	0.81	2.1E-08
PYN-2	50	30	20		6.2		1.8E-06	1.8E-2		
PYN-3	50	20	30		2.1		1.9E-06	5.7E-2		

60 rpm; 10 min of mixing were sufficient to generate a steady-state torque response, indicative of uniform dispersion of the components. From the material thus obtained, 1-mm thick sheets were compression rolled and subsequently machined to produce the samples for the respective tests.

Impedance and inductance complex-plane analyses were conducted in an Impedance Analyzer (Hewlett–Packard Model 4192 A), coupled to a computer (Model 9000-216) in the frequency range of 10–10^7 Hz. The samples were placed in a Variable Temperature Liquid Nitrogen Cryostat DN 1710 (Oxford Instrument Ltd) and the electrical contacts were made with fine silver wire and silver paste.

RESULTS AND DISCUSSION

The samples, the compositions of which are compiled in Table I, were analyzed by means of complex impedance spectroscopy as a function of temperature. The impedance spectra thus obtained were then processed through computer-assisted electrochemical data analysis software that calculates the equivalent circuit which ideally adjusts to the experimental data and determines the absolute value of each element (Table I).

Figure 1 shows the impedance spectra of each of the PP-copper composites analyzed at 303 K. For each experimental temperature an impedance spectrum is obtained similar to the one in Figure 1, enabling generalization.

The interpretation of these impedance spectra and their electrical characteristics supports the statement that these materials, independent of copper concentration, are essentially insulating, although a slight increase in conductivity is observed with increasing copper concentration. This trace of conductivity may be attributable to an incipient tunnel effect known[8] to allow the electrons to flow from one conductor particle to the next through the polymer film sandwiches between the particles, thus establishing an electric current. When this film is extremely thin, the optimum conditions are given for the electrons to flow through it as a consequence of the drop in electrical resistivity of the polymer between the two particles. The greater the thickness of this film, the less likely are the electrons to leap from one particle to the next, until at sufficiently great thicknesses no conduction at all occurs through tunnelling. Hence for these materials with a clearly capacitive behavior and minimal conductivity, the nonexistence of the tunnel effect is practically confirmed.

Due to their electrical characteristics an equivalent circuit is formed by means of parallel resistance and capacity (RC) (Fig. 1) on the impedance plane independent of copper concentration. The effect of

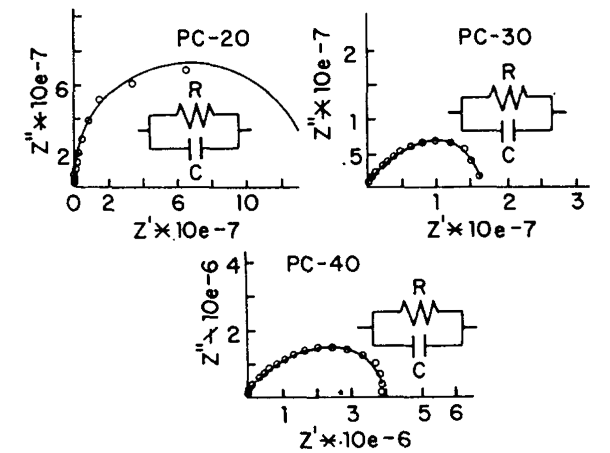

Figure 1 Impedance spectra of the copper composites.

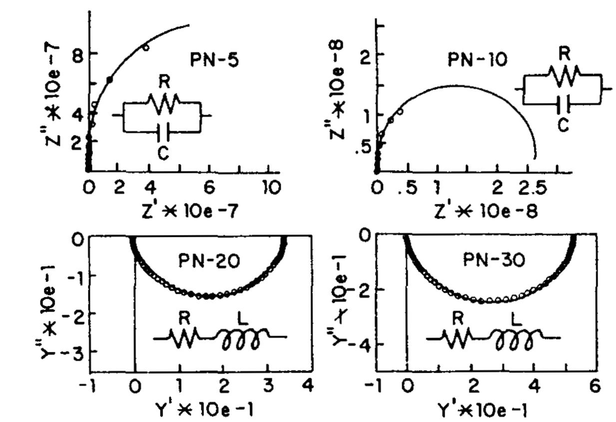

Figure 3 Impedance spectra of the carbon black composites.

temperature on certain conductive and dielectric properties of these materials may be seen in Figure 2 that shows electric decay occurring at close to ambient and is attributed to the different thermal expansion patterns of the polymer and the copper. Figure 2 indicates for each sample composition the temperature at maximum conductivity, maximum dielectric constant, etc.

A radically different situation occurs when analyzing the PP and carbon black (N) composites (Fig. 3). In these materials, when the PP incorporates low N content (5–10%) the situation is comparable up to a point to that of the copper composites, i.e. conductivity is fairly low, although there is a slight improvement when increasing the N portion to 10%. Hence an equivalent circuit of the RC type can be assigned in parallel on the impedance plane, which is typical of a basically capacitive material, as confirmed by the analysis of its electrical characteristics plotted against temperature in Figure 4, which shows the similarity to the copper composite plots. When N concentration is above 10%, a material is obtained with very high conductivity and an arc on the admittance plane (Fig. 3), which points toward a clearly pseudoinductive behavior and is typical of materials with a high electronic conductivity, such as metals. In fact the material obtained, when more than 10% N is incorporated into PP and YBaCuO composites, possesses all the electrical characteristics of metals, even the property of continually increasing conductivity with decreasing temperature (Fig. 4). This behavior is not found in semiconductor materials. The PP, YBaCuO, and N composites may be assigned an equivalent circuit which will depend on N concentration. Thus, while N concentration does not surpass the 10% threshold, the equivalent circuit will be parallel resistance and capacity on the impedance plane (RC), whereas the samples with higher N content present an equivalent circuit consisting of a resistance and a coil in series on the admittance plane (RL).

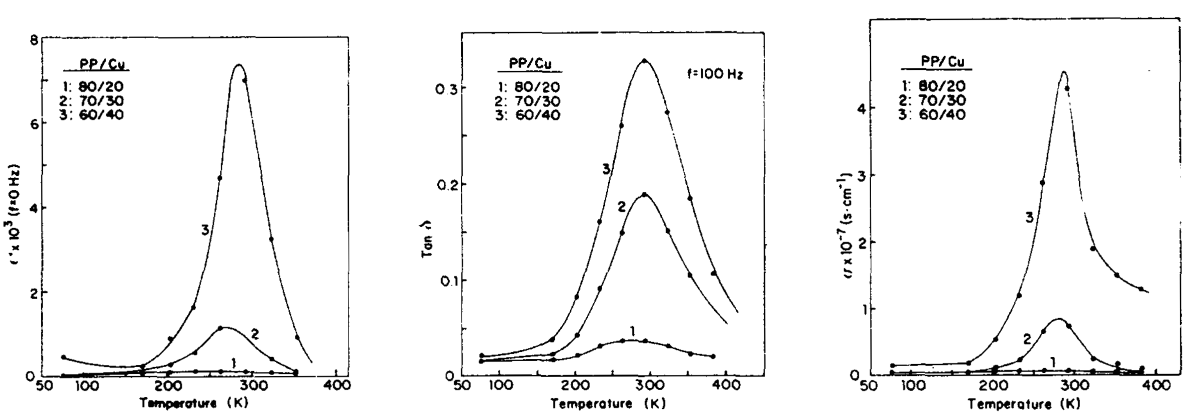

Figure 2 Temperature effect of the copper composites.

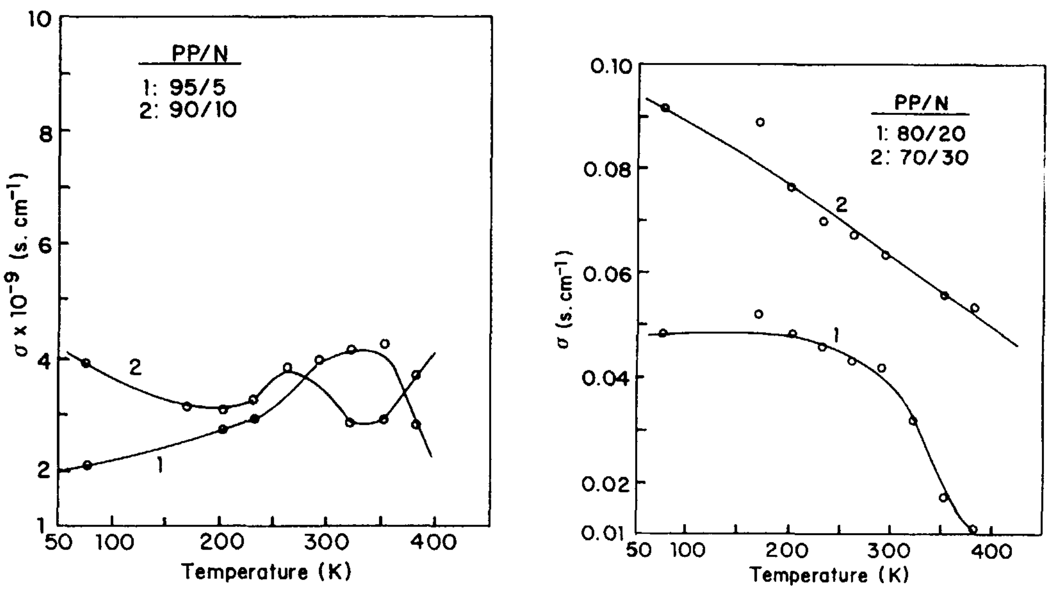

Figure 4 Temperature effect of the carbon black composites.

The electrical behavior of the binary composites consisting of PP and the superconductor ceramics YBaCuO is similar to that of the copper composites, the superconductivity value being practically negligible and without improvement with increasing YBaCuO content, even for very high Y concentrations (Fig. 5). This fact confirms that, in spite of the high YBaCuO concentration incorporable into PP, particle percolation is not achieved. They cannot even be brought close enough together to give rise to tunnel conduction. This condition can be explained molecularly in terms of the extraordinary affinity between YBaCuO and PP, which causes the YBaCuO particles (or part of the cluster) to surround themselves with a sufficiently thick polymer layer to inhibit electron passage by any means, and hence the material behaves like a perfect insulator. This fact was confirmed experimentally in our laboratories[8] by means of scanning electron microscopy (SEM). A material such as the one described has an equivalent circuit indistinguishable from those of copper composites, i.e. it possesses a resistance and a capacity in parallel on the impedance plane (RC), independent of the YBaCuO content of the sample. The effect of temperature on the conductive and dielectric properties of these materials (Fig. 6) demonstrates a behavior again is typical of insulating materials, presenting electrical transitions in the proximity of room temperature, essentially due to the different thermal expansion of the polymer on the one hand and the superconductor ceramics on the other.

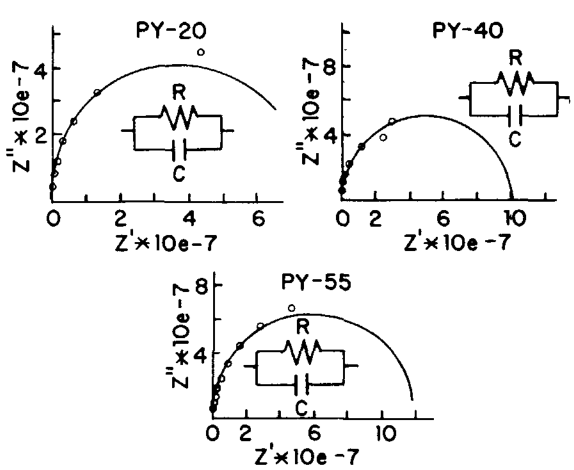

Figure 5 Impedance spectra of the YBaCuO composites.

When different amounts of copper are incorporated into PP and YBaCuO composites with the aim of improving their conductivity, the electrical properties of the resulting materials and the conduction mechanism vary, when comparing them to binary systems consisting of either PP/YBaCuO or PP/Copper (Fig. 7). Thus, with lower copper contents (up to 20%) the material behaves almost completely like a nonconductor judging by the conductivity values and the respective impedance spectra, the conductivity values fall within the limits of semiconductors as a consequence, either of the percolation (a mechanism to be discarded because the conductivity values ought to be higher) or the tunnel effect, whose latter explanation we support. In this latter case the presence of copper alters the affinity con-

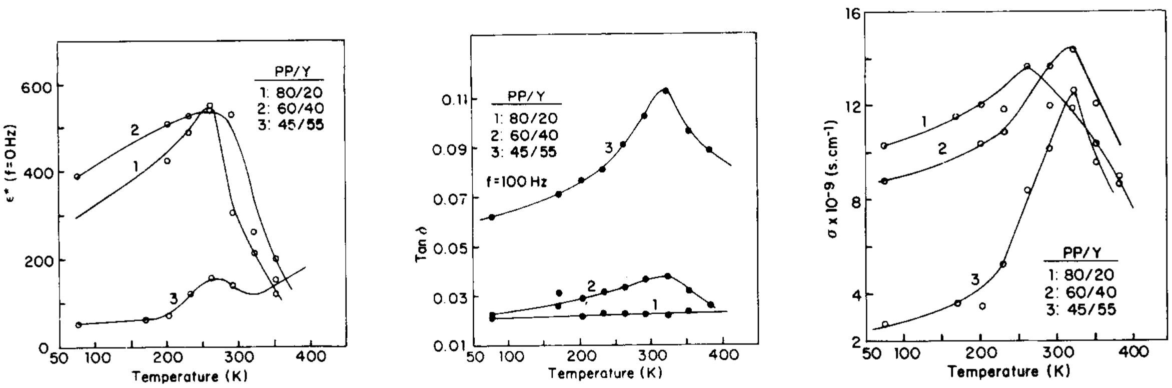

Figure 6 Temperature effect of the YBaCuO composites.

ditions between PP and YBaCuO and hence reduces the thickness of the film sandwiches between the PP and the conductor particles, a situation which would consequently favor a tunnel-type conduction. The equivalent circuit of these materials depends, as was stated above, on copper concentration. For low copper content the circuit is a resistance and a pure condenser in parallel when represented on the impedance plane (RC). At higher copper concentration, the circuit is a resistance and a constant phase element (CPE) in parallel on the impedance plane (RQ) with Y_0 and n values as indicated in Table I. Figure 8 shows the effects of temperature on the electrical characteristics.

When N is added to the PP/YBaCuO composite instead of copper, the electrical characteristics and the conduction mechanism of the material change again (Fig. 9). Thus, while for low carbon black content it shows a condensing or capacitive behavior with a conduction mechanism clearly assignable to tunnel-type conduction. With 10% N concentration, the conduction mechanism is the metal type displaying a pseudoinductive behavior typical of materials with high electronic conductivity, as supported by the steady increase in conductivity inversely proportional to temperature (Fig. 10). The equivalent circuit of these materials depends on N content, but for composites with less than 10% N, the equivalent circuit is a resistance and a constant phase element (CAPE) in parallel on the impedance plane (R), yielding Y and n values as indicated in Table I. With 10% N, the equivalent circuit turns out to be a resistance and a coil in series on the admittance plane (R) (Table I).

In Figure 11 the conductivity values of all the samples of our series are plotted against conductor filler concentration, based on the data obtained at ambient. The effect of carbon black and copper on the conduction mechanism of the binary system P/Abac (P) should be highlighted in particular. In both cases the presence of the filler radically changes the conductivity of the resulting materials, as a consequence of the changes brought about in the conduction mechanism. Copper proves capable of transforming the material (PIC) into a semiconductor, notably at higher filler volume; carbon black (PAN) converts it into an electronic conductor of the metal type.

CONCLUSIONS

The results obtained support the statement that the conduction mechanism of materials consisting of polymers and conductor particles, significantly depends on the affinity, wettability, and adhesion between the fillers and the polymers, taking into account that it is affinity that accounts for the three aggregate states, which may occur when incorpo-

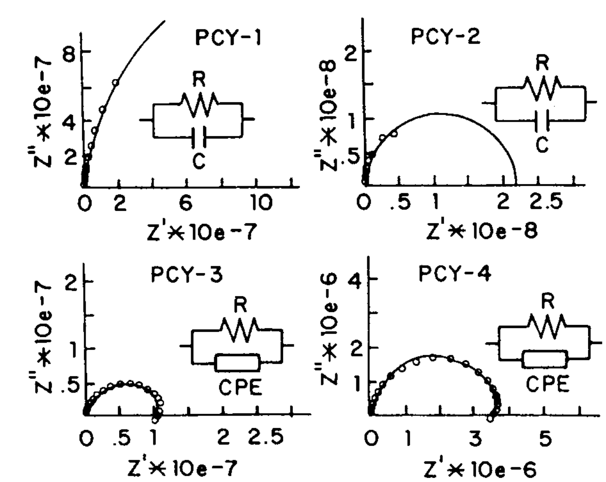

Figure 7 Impedance spectra of the copper/YBaCuO composites.

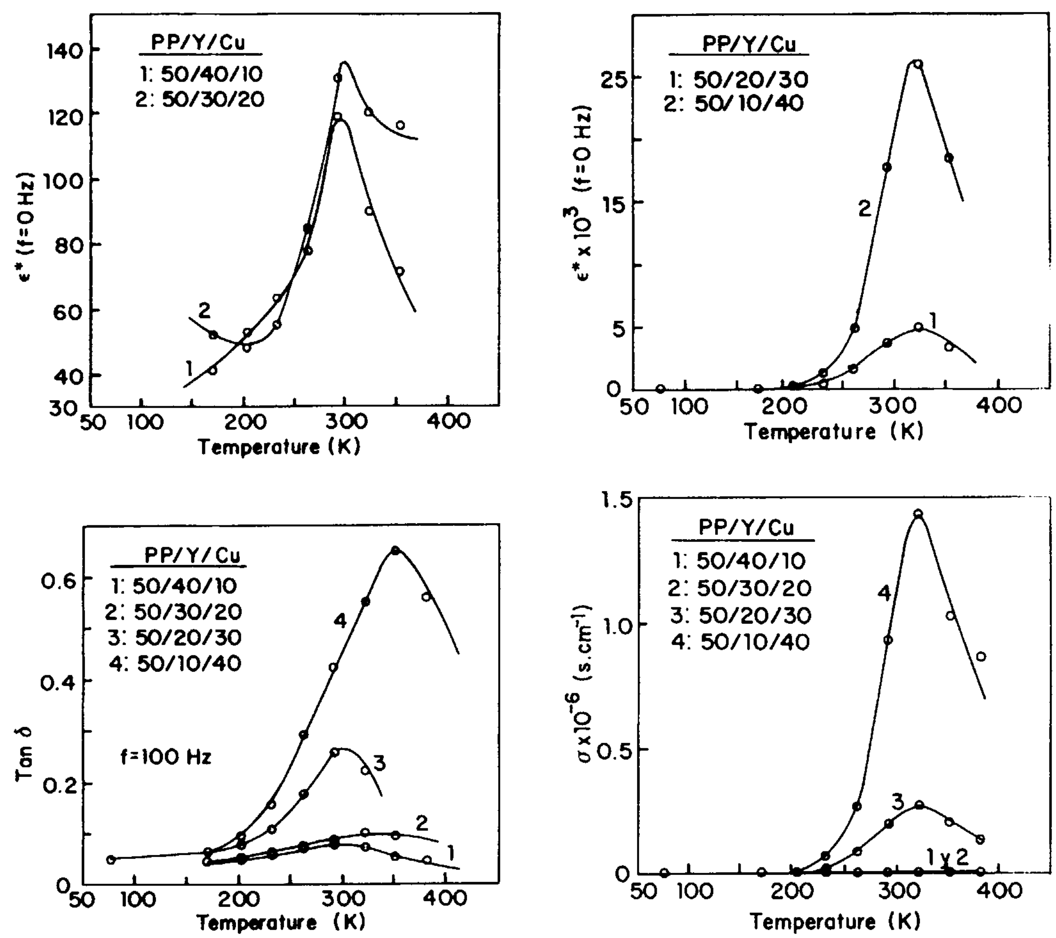

Figure 8 Temperature effect of the copper/YBaCuO composites.

rating fillers into polymers and which, at first sight, govern the conduction mechanism. The first of these states occurs for systems with little filler–polymer affinity, in which case, if the composite contains a sufficient amount of filler, the filler particles come into contact with each other (percolation) and the electrical current is established by means of an elec-

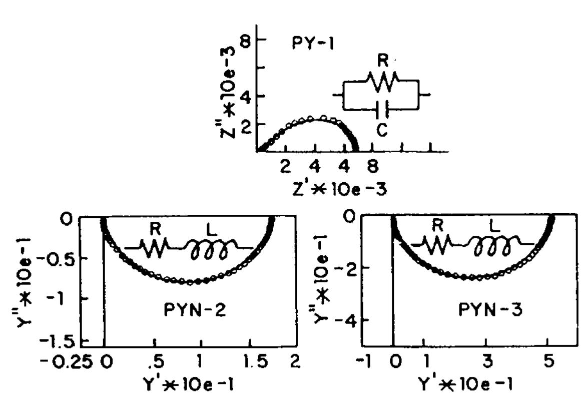

Figure 9 Impedance spectra of the carbon black/YBaCuO composites.

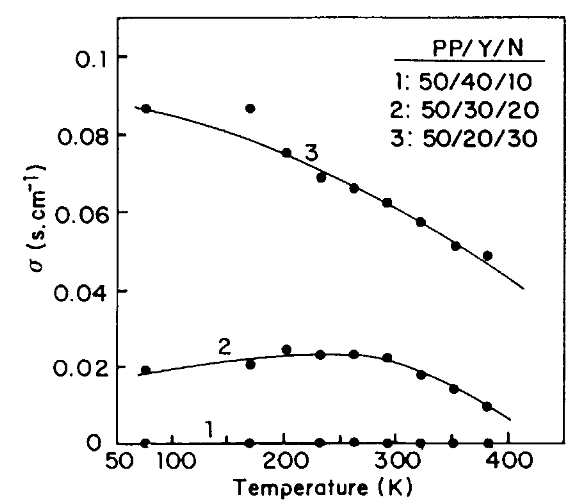

Figure 10 Temperature effect of the carbon black/YBaCuO composites.

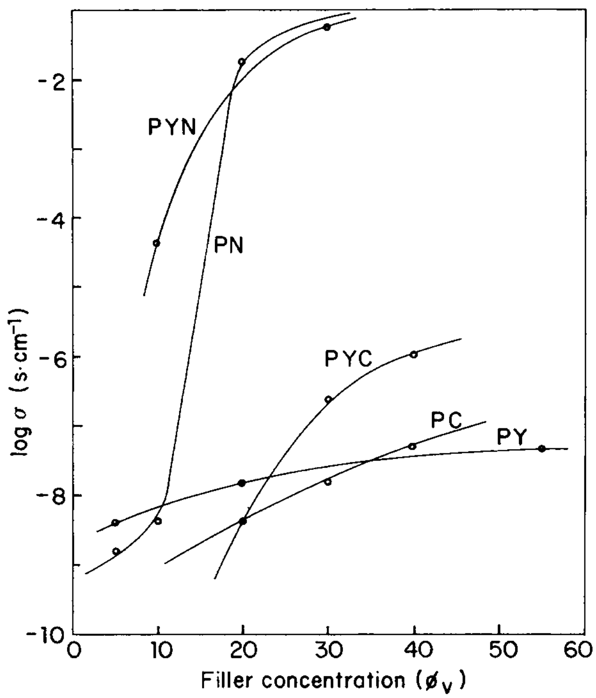

Figure 11 Conductivity values of the different composite families at room temperature.

tronic conduction mechanism (metallic conduction). In our series, the systems obeying this type of conduction are the binary PN and the ternary PAN systems at high N concentration. The second state applies to systems with higher filler–polymer affinity. The particles are no longer in contact, but surrounded by a fine polymer film and hence infinitesimal gaps among separate and adjacent particles may conduct an electrical current by a tunnel effect. This condition is fulfilled by the ternary PIC systems at the highest copper concentration. The third state holds for very strong filler–polymer affinity when the filler particles are insulated by and embedded in the polymeric matrix and hence prevent the electrons from skipping the gaps by means of the tunnel mechanism. This situation applies to the binary P and PC and the ternary PIC and PAN systems in the low filler content range.

In closing it should be emphasized that temperature only affects the absolute values of the elements of the equivalent circuit, but not the conduction mechanism.

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