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High T_c superconductor polymer composites based on $YBa_2Cu_3O_{7-x}$

Part I *Microstructure, conductivity and sinterization of PP composites*

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This work reports on the study of the microstructure and electrical properties (conduction and superconduction) of $YBa_2Cu_3O_{7-x}$ (Y) and polypropylene (PP) composites. For the purpose of enhancing and improving their conductive properties, different amounts of carbon black (N) and copper (Cu) were incorporated into these composites, and the effects of N, Cu and Y were determined, both on the microstructure of PP and on the electrical properties of the resulting composites. The complex systems on the basis of PP/Cu/Y and PP/N/Y were sintered in order to study their mechanical characteristics, their morphology and the superconductor properties of the end products.

1. Introduction

As a consequence of the discovery of superconductivity in certain oxides and sulphides below 10 K [1], several research groups succeeded in synthesizing new oxide-based superconductor materials [2–5], with increasingly higher critical temperatures. Nevertheless, the decisive breakthrough was brought about in 1987, when Wu *et al.* [6] found that the effect of substituting yttrium for lanthane in the then most powerful oxide blend known (LaBaCuO), was that the superconductor temperature T_c (critical temperature) of the resulting blend would rise remarkably, up to 93 K, which meant that the technological barrier set by the boiling temperature of liquid nitrogen (77 K) had been overcome.

The superconductor properties of this material (Meissner effect and zero resistivity below transition temperature) were strongly dependent on the synthesis conditions and on its morphology. At present this superconducting ceramic of a general formulation $YBa_2Cu_3O_{7-x}$ (henceforth YBaCuO) is being marketed as an industrial commodity, but its superconductor performance is not the best it could be. This is essentially due to the following: (i) Problems deriving from the intrinsic properties of the material with regard to their superconductor features, which means those referring to the low critical current density values at low fields, as found in YBaCuO, as well as to high frequency losses. (ii) Problems deriving from the mechanical properties of YBaCuO [7, 8] whose values are notably lower than those of conventional metallic superconductors (Nb_3Sn and NbTi). Even worse, they are so brittle that they cause practically insoluble problems when they are to be moulded and die-cast into pieces of even the simplest shapes. Occasionally circumstances require them to be incorporated into high conductivity metallic matrices (generally copper), thus creating new technological problems. (iii) Problems deriving from the scarce stability of these materials in relatively conventional environments, which causes the materials to degrade with relative ease.

The solution to these problems is being approached at present in a decisive way: for instance, the research groups headed by Duran [9] and Carreras [10] are making tremendous efforts to improve the intrinsic properties of the material, to raise the critical current density values and to eliminate, as far as possible, the high frequency losses, having already achieved a number of successful results. The problems of manufacture, mechanical properties and chemical environmental stability have been given tentative solutions in the form of impregnation or incorporation of superconducting ceramics into polymeric matrices [11–13]. Optimum properties have, however, not yet been accomplished in the resulting composites (especially from a superconductor point of view), because to date none of the experimental polymeric systems has proved capable of favouring particle interconnectivity and/or potential electrical conductivity through a tunnel mechanism [14, 15].

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On these lines and in this the first paper of a series, the authors have chosen polypropylene as the basic polymeric system to be blended with YBaCuO. By the same token and in order to favour interconductivity, superconducting ceramics have been incorporated in amounts above the miscibility threshold, without producing any deteriorating effect on the mechanical properties of the composites. In addition and to the purpose of enhancing conductivity, conducting fillers of the carbon black or copper type were incorporated in powder form into the system PP/YBaCuO. In general terms, this work relates to the analysis and characterization of the structure, morphology and conductor or superconductor properties in the composites, as well as in their sintered products, with the aim of gaining insight into the effects exerted by the components on the properties of either type of material.

2. Experimental procedure

The following raw materials were used in the experimental composites: high-T_c-superconductor powders Superamics Y 200 (< 25 μm) were 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 (W 60), preheated to 473 K. Rotor speed was set at 60 r.p.m.: Ten minutes of mixing were sufficient to generate a steady state torque response, indicative of uniform dispersion of the components. From the materials thus obtained, 1 mm thick sheets were compression-rolled and subsequently machined to produce the samples for the respective tests.

The samples were sintered according to the following heat treatment programme. The platinum boat containing the 1 mm-thick parallelopipedic sample was placed in an oven with programmed heating/cooling rates. During a first stage the sample is heated to 500 °C at a rate of 1 °C min^{-1}, holding it at that temperature for one hour. During the second stage the temperature is raised to 930 °C over a period of two hours, at which temperature the sample remains for another four hours. Subsequently it is cooled down to 500 °C at a rate of 1 °C min^{-1}, where it is held for eight hours, after which time it is cooled to room temperature at a rate of 1 °C min^{-1}.

Isothermal crystallization from the melt was studied using a Perkin Elmer DSC 7 differential scanning calorimeter operating under N_2 atmosphere. Electron microscope observation was carried out with a Zeiss scanning electron microscope (SEM), model DMS 950. Impedance and inductance complex-plane analyses were conducted on an impedance analyser (Hewlett Packard, model 4192A), computer-aided (model 9000-216), in the frequency range of 10 to 10^7 Hz at room temperature. Electric reactivity was measured from room temperature to 77 K (the boiling point of liquid N_2) using a four point d.c.-probe method. Electrical contact was made with a fine silver wire and silver paste. A constant current of 100 mA was established for resistance measurements. The changes in resistivity with temperature were monitored continuously using an X–Y recorder. X-ray diffraction (XRD) of the samples was obtained with a Sieman's D-500 diffractometer using a Ni-filtered CuK_α X-ray beam excited at 40 kV.

3. Results and discussion

3.1. Unsintered composites

The crystalline microstructure of the different composites was determined by means of the isothermal crystallization kinetics using Avrami's equation [16]

$$X_T = 1 - \exp(-Kt^n) \qquad (1)$$

where X_T is the weight fraction of the crystallized material at time t; K stands for the overall kinetic rate constant and n is the Avrami exponent, which depends on the type of nucleation and geometry of the growing crystals. The K and n values were calculated for each T_c (crystallization temperature) from the slope and the Y-intercept of the straight lines obtained by plotting $\log(\ln(1 - t))$ versus $\log t$.

Table I shows the kinetic data obtained from isothermal crystallization of the different composites at 401 K. Fig. 1 presents the variation of T_m, K and n as a function of conducting filler portion for each family. The results obtained allow for the following statements

TABLE I Isothermal crystallization at 401 K of the composites. Kinetics data

Samples	Composition				T_m (K)	log K (Min)	n
	PP (% vol.)	Cu (% vol.)	N (% vol.)	YBaCuO (% vol.)			
PP	100				437.7	− 2.429	2.77
PC-20	80	20			438.8	− 0.775	2.81
PC-30	70	30			438.4	− 0.083	2.56
PC-40	60	40			439.1	− 0.325	2.76
PN-5	95		5		438.8	− 1.871	3.08
PN-15	85		15		439.1	− 0.721	2.97
PN-30	70		30		438.4	− 0.523	2.91
PY-20	80			20	437.3	− 1.612	2.93
PY-40	60			40	432.6	− 2.311	2.49
PY-55	45			55	429.9	− 0.742	2.11

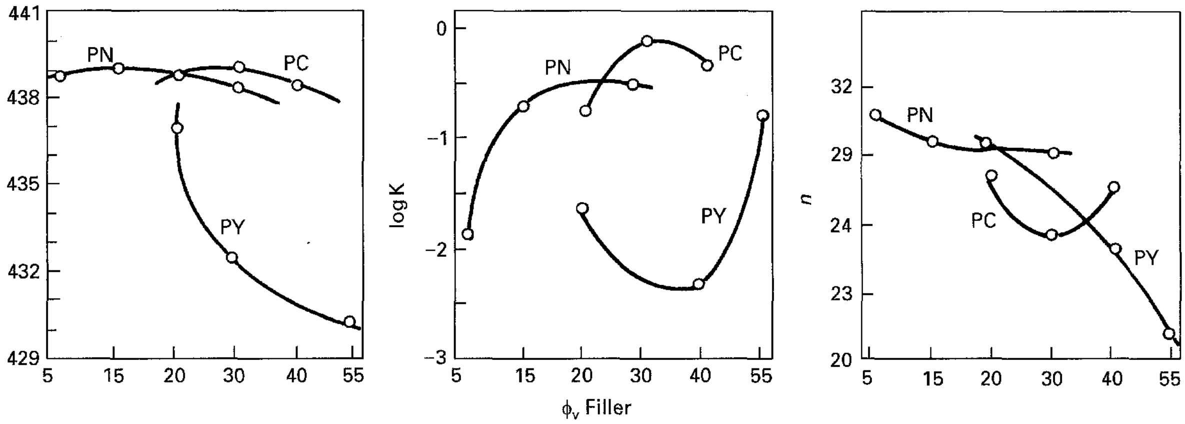

Figure 1 Kinetic data as function of conducting filler for each family.

1. The melting temperatures of the carbon black and copper filled composites are practically independent of the filler portion present in the blend. In contrast, the YBaCuO composites are composition-sensitive, and their melting point drops drastically with increasing YBaCuO concentration.

2. The isothermal crystallization rate of the carbon black and copper composites increases consistently proportionate to increments in conducting filler concentration. The YBaCuO composites, however, show a valley around 40% concentration. In addition, when comparing the carbon black, copper and YBaCuO composites for the same filler portions, YBaCuO proves to trigger the lowest isothermal crystallization rates of PP, whereas copper produces the highest.

3. The effect of the filler on the crystal growth geometry of PP can be seen in Fig. 1c. It shows a practically tridimensional growth geometry for the carbon black composites ($n \sim 3$), independent of carbon black content, whereas YBaCuO composites prove to be strongly dependent on YBaCuO concentration, approaching practically bidimensional growth geometries ($n = 2$) for YBaCuO volume fractions above 55%. The copper composites present growth geometries intermediate between the former two.

These totally diverging effects exerted by carbon black, copper and YBaCuO on the isothermal crystallization of PP, when the aforementioned fillers are present in isolation in the different composites, are due, fundamentally, to the existence of PP-filler interactions whose nature varies according to the type of filler used, as demonstrated by the morphological analysis of the samples by SEM, as well as by the conductivity measurements to be discussed below.

Regarding the morphological analysis of the samples, SEM, as shown in Fig. 2, proved the carbon black and copper composites to possess good homogeneity and connectivity between the particles, as a consequence of less good filler–polymer adhesion (in this case the crystalline structure of PP would develop in the polymer itself without any influence from the filler). In the case of YBaCuO composites, however, (Fig. 3), the adhesion between the superconductor ceramics and the polymer is so strong that the formation of a kind of mesophase is induced, which surrounds the particles in such a way that both the crystalline structure of PP and the crystallization rate in this mesophase are strongly influenced by the surface activity of the filler, whose interaction with the polymer is very intense.

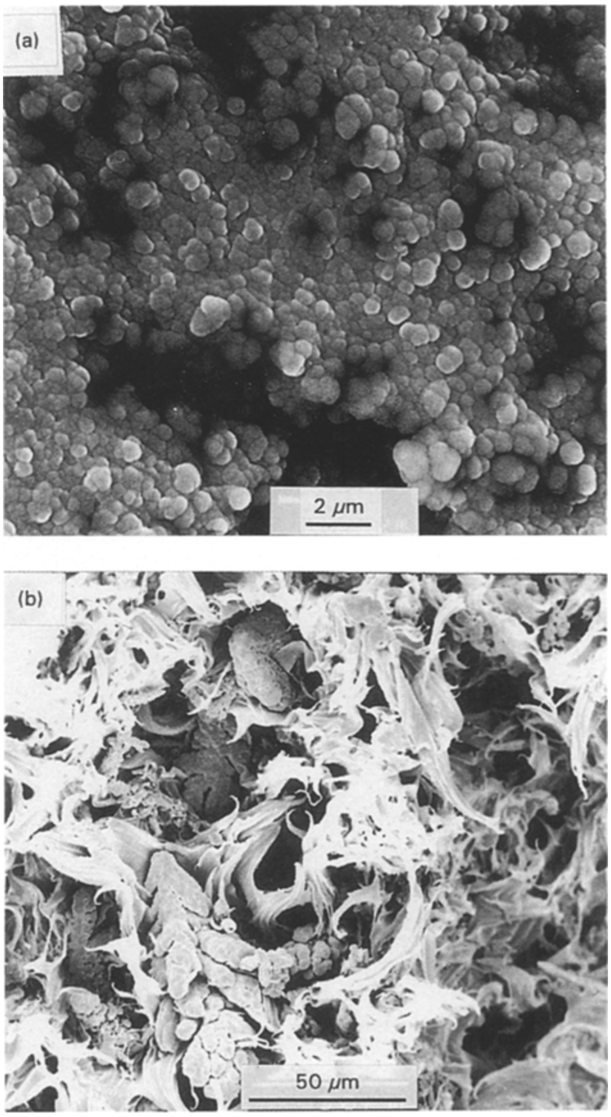

Figure 2 SEM of (a) carbon black and (b) copper composites.

In the light of our discussion it is now understood that the different degrees of adhesion between the polymer and the conductor fillers affect particle interconnectivity and hence their electrical conductivity, as will be shown in what follows.

As pointed out in the Introduction, one of the solutions at hand to facilitate conduction through the composite, when perfect particle interconnectivity of the superconductor ceramics does not exist, would be to incorporate different amounts of conducting additives, such as finely ground carbon black or metallic copper, into the basic composite system of PP/YBaCuO with a high ceramic concentration, in an attempt to potentiate conduction and superconduction in the resulting materials.

In the first case the composites were synthesized whose composition, conductivity and permittivity values are compiled in Table II. The plots of conductivity against YBaCuO concentration of each family are shown in Fig. 4. The interpretation of these data allows us to conclude that the conductivity of the system PY, apart from being very low (almost at the threshold of insulating systems) remains constant with increasing superconductor ceramic concentration, even for the highest concentration recorded. This fact clearly demonstrates that particle interconnectivity (percolation) does not exist here, as a consequence of the strong adhesion to the polymer, which causes all the particles to be coated with an insulating layer, thus inhibiting the transfer of the electric charge through the material. Percolation being non-existent, particle interconnectivity could still take place through a tunnel-type mechanism. Yet this mechanism is not feasible in our composites (as can be inferred from the conductivity data in Table II), because for this tunnel mechanism to become effective the maximum distance between the particles should not exceed 10 nm [14, 15]. In our composites, however, the particles are separated by an insulating polymer layer which is considerably wider (Fig. 3).

Copper incorporation into the system PP/YBaCuO does not accomplish any improvement in the conductivity of the resulting composite; in fact it diminishes it (system PYC in Fig. 4). The presence of carbon black, however, improves conductivity spectacularly (system PYN in Fig. 4), and this is strictly proportionate to filler portion. Carbon black concentrations of 30% volume convert the resulting composite practically

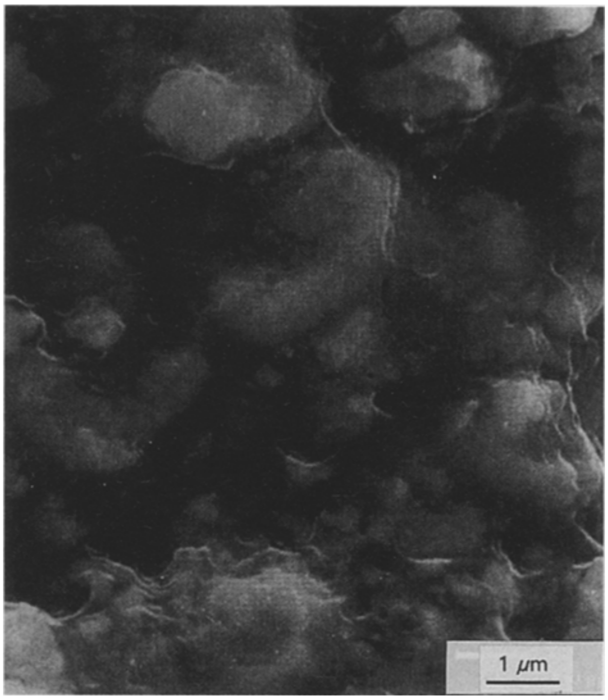

Figure 3 SEM of YBaCuO composites.

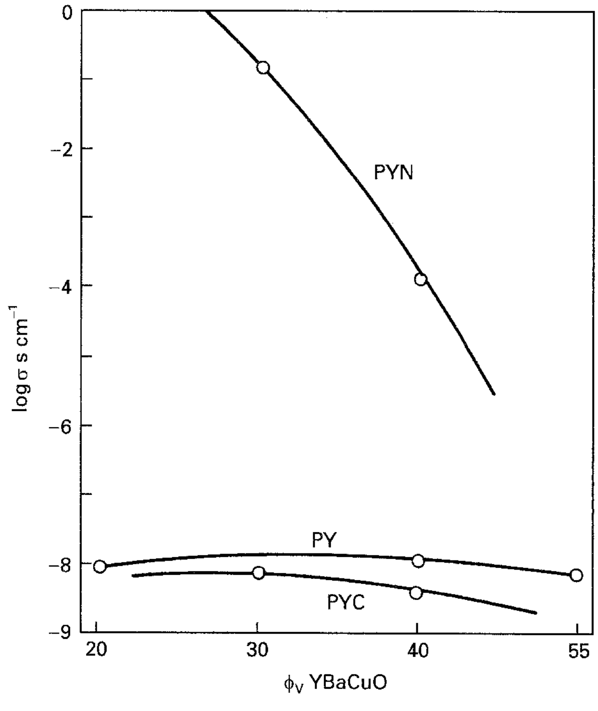

Figure 4 Conductivity of PY composites as function of YBaCuO concentration. T = 293 K.

TABLE II Composition, conductivity and permittivity at 401 K of the composites.

Samples	PP % v	YBaCuO % v	N % v	Cu % v	E (f = 0)	log Cond. s.cm^{-1}
PY-20	80	20			305.6	− 8.058
PY-40	60	40			530.1	− 7.861
PY-55	45	55			142.7	− 7.991
PYN-1	50	40	10		2604800	− 3.793
PYN-2	50	30	20		*	− 0.767
PYC-1	50	40		10	130.2	− 8.302
PYC-2	50	30		20	118.6	− 8.057

* Induction.

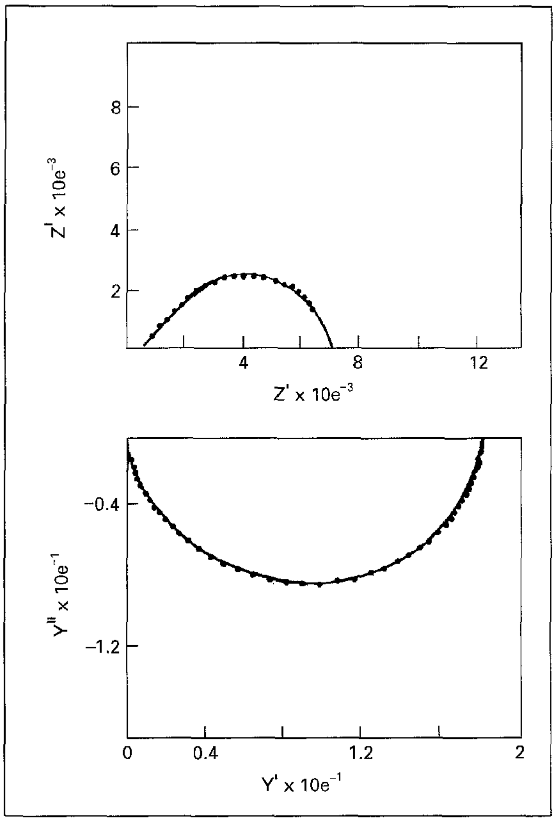

Figure 5 Impedance spectroscopy analysis of the samples at 401 K. (a) PYN-1; (b) PYN-2.

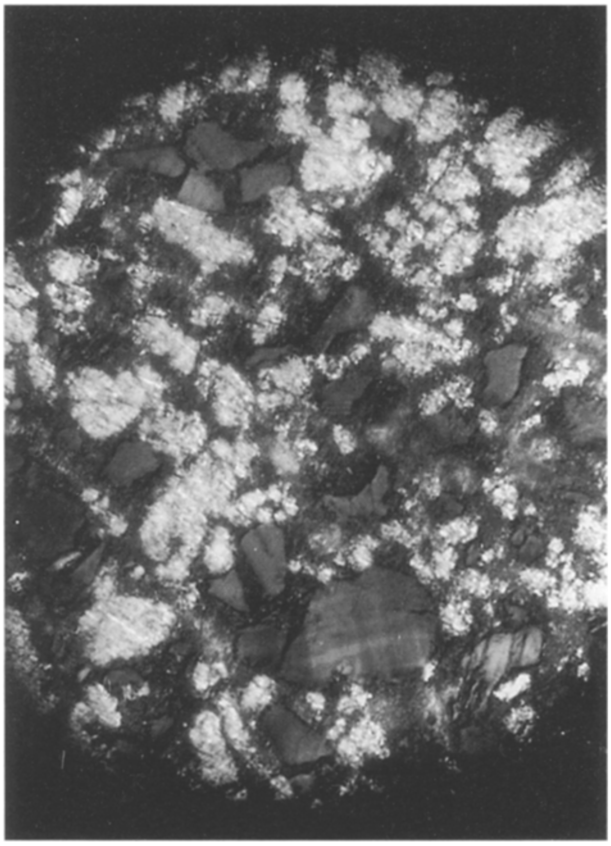

Figure 6 ROM of the sample at 401 K.

into a metal, with its respective inductive properties, as indicated by the admittance arc of sample PYN-2 in Fig. 5a. The other samples present an impedance arc similar to the one shown in Fig. 5b, whose composition is the same as that of the inductive system PYN-2, yet with a lower carbon black portion.

All the composites obtained were analysed as to their superconductor character, in order to determine their superconductor transition temperature by means of experimentally determining their resistivity as a function of temperature. In conventional superconductor composites there exists a brusque drop in resistivity, when the critical transition temperature (T_c) is reached, at which point the resistivity value of these materials is zero. In none of the experimental samples a superconductor transition temperature was detected, which fact may be indicative of two alternative explanations: either the ceramic, in the course of the blending and machining processes, has lost its superconductor properties, or else the YBaCuO particles are not percolated and hence electric charge transfer through the material does not exist. The first hypothesis has to be discarded, on account of the presence of "twinning" in the YBaCuO crystals occluded in the polymeric matrix (Fig. 6), which is irrefutable evidence of the superconductor character of the YBaCuO particles. The micrograph reproduced in Fig. 6 was produced by reflection optical microscopy (ROM) after optical etching of the polished samples.

Confirmation of the fact that the YBaCuO occluded in all the experimental samples continues to be a superconductor, as well as the non-detection of superconductor transitions in the systems under study, allows for the inference that the composites obtained are superconductors from a magnetic point of view (they exclude the magnetic field), but they are not compliant in electrical terms, i.e. they do not conduct the electric current with zero resistivity below their superconductor transition temperatures.

3.2. Sintered composites

The different complex systems obtained, consisting of PP, YBaCuO and different superconducting filler concentrations were subjected to a sinterization process, with the aim of determining whether the resulting products were better performers or not from a mechanical and superconductor point of view, as compared to sintered YBaCuO products in the absence of polymer and/or conductor additives. The approach taken in this part of our research started out by determining the orthorhombicity parameter [17]

$$\sigma = 100\left[\frac{2(b_0 - a_0)}{(b_0 + a_0)}\right] \tag{2}$$

and the oxygen content [18]

$$X = 7.64 - 0.595\,C_0(\text{nm})$$

of the sintered samples by means of X-ray diffraction analysis, on the grounds that these parameters fully distinguish a superconductor YBaCuO (orthorhombic), from a non-superconductor (tetragonal). For a YBaCuO to be a superconductor, the orthorhombicity parameter must range between 2 and 1.3, and the oxygen content between 7 and 6.8.

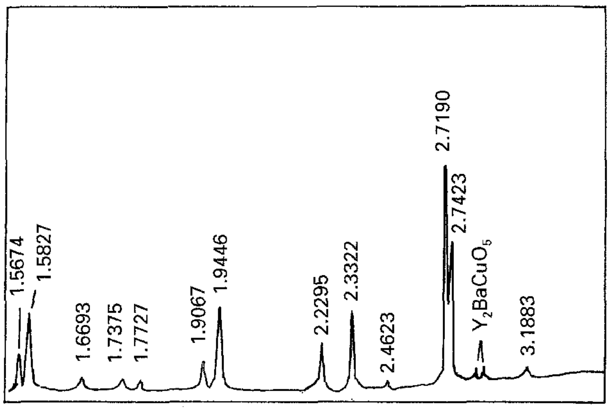

Figure 7 X-ray diffraction diagram of the PYC-1 composite.

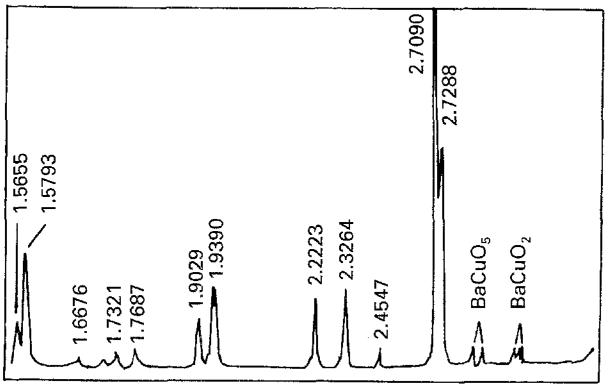

Figure 8 X-ray diffraction diagram of the PYN-1 composite.

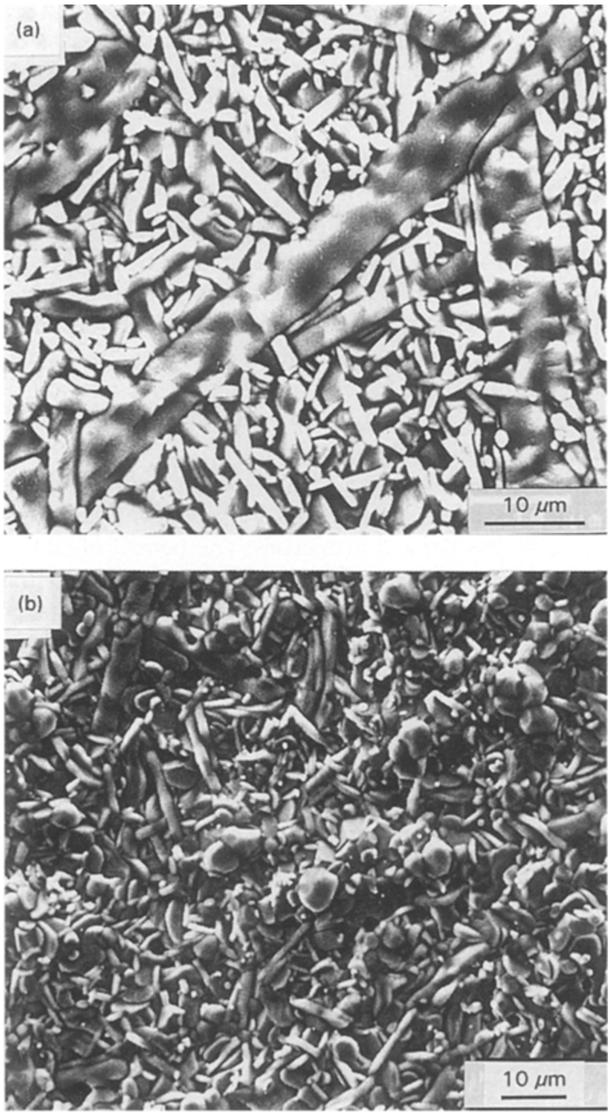

Figure 9 SEM of the sintered samples of (a) PYN and (b) PYC composite.

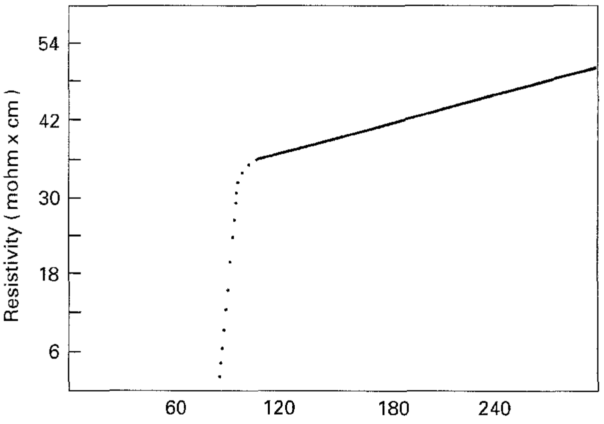

Figure 10 Resistivity against temperature of the PYC-1 sintered composite.

Fig. 7 shows the XRD diagram of sample PYC-1, whereas Fig. 8 reproduces that of sample PYN-1. In both figures clearly orthorhombic phases can be detected, as well as traces of BaCuO and a green phase of Y_2BaCuO_5. In addition, PYC-1 shows a well-defined peak corresponding to the presence of CuO.

From the respective X-ray diffractograms both the orthorhombicity parameter of the two samples and their oxygen content were determined. Sample PYC-1 has an orthorhombicity parameter of 1.97, its oxygen content amounting to 6.95, whereas the values for sample PYN-1 are 1.92 and 6.91, respectively. Hence it is legitimate to assume that the two samples present the orthorhombicity symmetry of YBaCuO with similar degrees of asymmetry.

SEM analysis of the two sintered samples (Fig. 9) indicates that the system PYN is a material consisting of acidular grains with highly hyperbolic growth regions (crystals, several tens of μm in length), but also showing other areas with a certain degree of preferential orientation. The sintered PYC system presents a similar microstructure, except for lower growth in the grains.

These data enable us to confirm that the materials obtained via sinterization of the PYC and PYN composites are superconductors with similar characteristics. In the endeavour to provide conclusive and definite evidence of the superconductivity of these samples the necessary assays were conducted to determine the critical transition temperature of one and the other system. These assays included resistivity analysis of the samples as a function of temperature (Fig. 10) using a four-point d.c.-probe technique and employing a constant current source to inject a 10 mA signal. For voltage measurements in the internal electrodes a digital microvoltmeter with high internal resistance was used. As can be seen in Fig. 10, which shows the

PYC-1 sample (a similar behaviour was recorded for the system PYN-1), the material tested proves to be a superconductor composite with a critical temperature of 90 K.

4. Conclusions

Carbon black and copper have proved to be additives which enhance and improve the conductivity of polypropylene and YBaCuO composites containing them. They are, however, incapable of converting the resulting complex composites into a superconductor system.

In contrast, the sintered products of the previously obtained complex systems are superconductor materials with a $T_c = 90$ K, independently of whether they derive from a system filled with carbon black or copper, both products generally possessing fairly acceptable mechanical properties. The benefit of sintering complex PP/YBaCuO composites resides in the ease with which they can be given the desired shapes and that they can be relied on to keep these shapes after sinterization.

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