Extrinsic Conducting and Superconducting Polymer Systems. III. Electrical Properties of PVDF/PS Blends Containing Copper, Carbon Black, and YBaCuO Fillers

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SYNOPSIS

In this work, the electrical characterization of three extrinsic polymeric conducting systems was carried out using complex impedance spectroscopy. These systems were obtained by the incorporation of conducting fillers (carbon black and metallic copper), on the one hand, and, on the other hand, by blending with a superconducting ceramic (YBaCuO). The experimental results prove that the electrical characteristics of these systems vary as a function of the nature of the filler added. In the case of metallic copper, the resulting composites possess a conductivity which is intermediate between insulating materials and semiconductors. When carbon black is incorporated in concentrations above 10%, the composites may be considered as metalliclike from the point of view of conductivity. Finally, when the filler is YBaCuO, the low conductivity values obtained are indicative of insulating materials regardless of their composition. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Extrinsic conducting systems[1-6] are of considerable importance in electrical and electronic industries, as they are capable of solving two types of problems: The first of these relates to the miniaturization of electronic circuits and circuit multiplication in any appliance, which causes parasitic electromagnetic noise to appear over the whole Hertzian frequency range, thus interfering electromagnetically with the system and, hence, preventing information from circulating correctly through the habitual channels. One of the fields most severely affected by this problem is that of computers, where data protection and confidentiality are indispensable. This electromagnetic noise can be suppressed by coating components and circuits with materials capable of absorbing these waves and extrinsic conducting polymers have proved to be especially appropriate in this case as low conductivities (10^{-2}–10 S cm^{-1}) are needed. The second problem which may be solved by using extrinsic conducting polymeric systems is derived from the existence of electrostatic loads which may appear in component environments during handling and/or operation. These loads generate sufficiently intense magnetic fields to make the component useless. To dissipate these loads, protective coating materials have to be employed whose conductivity ranges between 10^{-4} and 10^{-1} S cm^{-1}.

Apart from the aforementioned applications, a number of others exist which are of a strategic nature as a consequence of the capacity of these materials to absorb microwaves. Materials possessing a conductivity between 10^{-1} and 10^{1} S cm^{-1} are capable of absorbing waves in the gigaHertz frequency range, i.e., the frequency used for radar emissions. For instance, polymers filled with certain ferrooxides constitute one of the approaches presently under study to ensure invisibility against the radar scans of military facilities.

In this work, which expands on previous research,[7,8] these systems as well as those resulting from incorporating the superconducting ceramics YBaCuO into the polymeric matrix are being characterized from an electrical point of view. The electrical study is conducted using complex impedance spectroscopy and will serve as a basis and input to an ensuing assessment of the superconducting

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properties of a series of composites obtained by YBaCuO incorporation into certain conducting systems, such as PVDF/PS/carbon and PVDF/PS/copper, whose results will be reported on in forthcoming work of this series.

EXPERIMENTAL

The materials used were two conventional polymers: poly(vinylidene fluoride) (PVDF) supplied by Solvay under the trade name Solef 6010 ($M_w/M_n = 4.5$) and polystyrene (PS) polystyrol 143E from BASF ($M_w = 200,000$). The conducting fillers used were carbon black (CB) Isaf N200 supplied in powder form (20 nm) with a density of 1.8 g/cm^3 by Cabot Laboratories and metallic copper (Cu) from Merck, also in powder form with a grain size of 63 μm and a density of 8.9 g/cm^3. The superconducting ceramic was YBa2Cu3O7-x Superamic Y200 supplied by Rhône Poulenc, with a grain size below 35 μm and a density of 6.3 g/cm^3.

Component blending was carried out in a Brabender torque rheometer. To optimize the dispersion, several factors were taken into account: a sufficient total blend volume to fill the mixing chamber completely, adequate temperatures to soften and melt the materials without degrading them, and a rotor rate appropriate to ensure optimum shear. The mixing chamber was a W 60 type, the temperature was set initially at 468 K, and the rotor rate was 55 rpm; the blend remained in the chamber for 10 min once the torque had stabilized.

Electrical characterization was carried out using complex impedance spectroscopy. Sample pellets (diameter 1 cm, height 0.1 cm) were prepared in a Collin press. The top and the bottom of the pellet were then coated with an Ag film (Lustre Ceramico 200 supplied by Emetron) to ensure good contact between the sample surface and the measuring electrode. Measurements were conducted with a Hewlett-Packard impedance analyzer HP 4192A LF; the frequency range was 0.01–10,000 kHz and the measurement temperature 298 K. The voltage applied was constant for each measurement, but varied according to the material type, ranging from 0.1 to 1 V.

RESULTS AND DISCUSSION

Complex impedance spectroscopy yielded complex plane impedance (ρ) arcs for the different PVDF/PS/Cu samples as represented in Figure 1, where

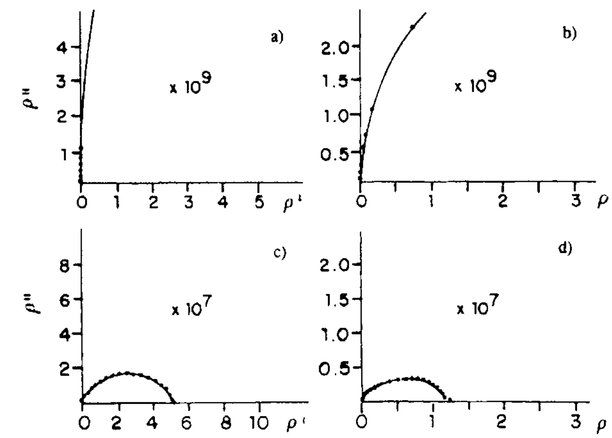


Figure 1 Impedance arcs at 298 K of copper-filled systems with a ratio PVDF/PS 70/30 and different copper concentrations (%ϕ_v): (a) 2; (b) 10; (c) 30; (d) 35.

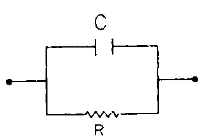
the evolution of the impedance arc is shown to be a function of the concentration of the conducting additive. These arcs allow all the electrical characteristics of these systems, as compiled in Table I, to be determined. For each blend composition, the arc is observed to "close" with increasing copper concentration, which is indicative of a significant increase in conductivity, as confirmed by the absolute conductivity value listed in Table I. Nevertheless, one aspect should be especially highlighted: Generally, when a single and homogeneous conducting phase exists, the arc forms a perfect semicircle with a well-defined center, either directly on the abscissa or outside it. At the highest copper concentration, there are samples which exhibit two more or less overlapping arcs, which is indicative of the existence of two different conducting phases. As this is present only at the highest filler concentration, it is envisaged that this is due to a nonhomogeneous distribution of the filler in the polymeric matrix, which results in two contributions to total conductivity: one derived from the copper agglomerates which doubtlessly exist and another derived from the less densely clustered copper particles.

Based on the data obtained for each of the samples, Figure 2 shows the variation of the dielectric constant (ϵ'), the loss tangent ($\tan \delta$), and conductivity (σ) as a function of copper concentration. Both ϵ' and $\tan \delta$ prove to be relatively sensitive vis-à-vis copper concentration and blend composition. For instance, the dielectric constant increases in direct proportion to the copper concentration. In contrast, for one and the same copper concentration, it diminishes with an increasing PS portion in the polymeric matrix. A similar behavior can be observed for the loss tangent, which increases with copper

Table I Electrical Properties of Copper-filled Systems

Composition % ϕ_v				
PVDF/PS	Cu	σ (S cm^{-1})	ϵ' $\omega = 10^5$ Hz	tan δ $\omega = 10^5$ Hz
100/0	2	1.273 E-10	11.3	0.080
	10	1.271 E-10	15.5	0.052
	30	1.189 E-08	46.0	0.143
	40	7.456 E-07	67.5	0.580
70/30	2	1.270 E-10	9.0	0.030
	10	1.269 E-10	12.9	0.053
	30	1.944 E-07	45.0	0.480
	35	8.088 E-08	61.2	0.231
50/50	2	1.281 E-10	6.54	0.014
	10	1.274 E-10	9.3	0.044
	30	1.117 E-07	41.8	0.299
	35	6.278 E-08	43.1	0.193
30/70	2	1.281 E-10	6.2	0.009
	10	1.272 E-10	8.6	0.048
	30	1.080 E-07	30.4	0.229
	35	1.812 E-08	35.0	0.176

concentration, until it reaches a certain threshold, as of which tan δ decreases drastically, as a consequence of material heterogeneities. The conductivity also increases as a function of copper concentration. The peak value reached is not very high and is independent of the polymer ratio in the blend, which supports the hypothesis that these materials are on the borderline between insulating and semiconducting materials. Their equivalent circuit corresponds to a resistor and a capacitor placed in parallel on the impedance plane, as confirmed by Boukamp's program of equivalent circuit adjustment[9]:



Under these conditions, the conduction mechanism for all copper composites takes place by means of the tunneling effect and never through percolation, as would have been expected, taking into account the high conductivity of copper and the high copper concentration in certain samples. This behavior originates from a "wettability" problem of the filler by the polymer, which prevents the particles from crosslinking or continuous multicontact.

The scenery changes completely when dealing with the system PVDF/PS/CB, whose analytical results are compiled in Table II. The arcs obtained for the different samples by complex impedance spectroscopy are shown in Figure 3, which shows that carbon black is the variable which produces major changes, both in the shape of the arcs and in the conductivity values. All the sample families of

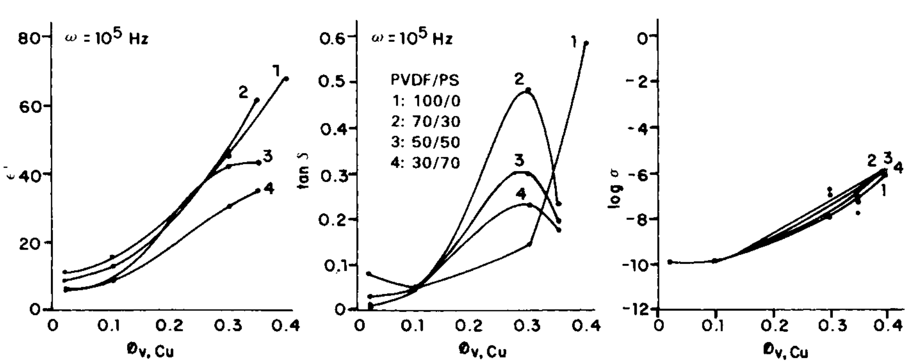


Figure 2 ϵ', tan δ, and σ as a function of copper content for PVDF/PS/Cu systems.

the system PVDF/PS/CB go through the same stages: At low carbon black concentration (2%), the composites practically behave like an insulating material with an equivalent circuit consisting of a resistor and a capacitor in parallel on the impedance plane, similar to the behavior obtained for the PVDF/PS/Cu system throughout.

At 10% carbon black concentration, conductivity increases spectacularly (in some cases up to 1 million times), except for the sample with the highest PS content. The 10% CB samples present an equivalent circuit similar to the one described for the lower concentrations, except for the values R and C which are distinctly smaller. With 30% CB concentration, the most drastic changes can be observed: The experimental materials present an arc on the admittance (Y) plane, which is indicative of a high conductivity and a considerable inductive effect. These are, in fact, materials which, from the point of view of conductivity, resemble metals and present an equivalent circuit consisting of a resistor and an inductance coil placed in series on the admittance plane, as was confirmed by the adjustment program used[9]:

Figure 4 shows conductivity plotted against CB concentration. CB particle crosslinking takes place at a certain filler concentration, which at the same time is a function of PS content in the blend. Thus, at higher PS concentrations, the percolation threshold rises and the conductivity diminishes for one and the same filler concentration. The conduction mechanism is a function of CB concentration, but in general terms (and at 10% CB), the mechanism is clearly percolative, due to the fact that the polymeric system does not constrain particle interconnectivity, contrary to what occurred in the case of copper-filled composites.

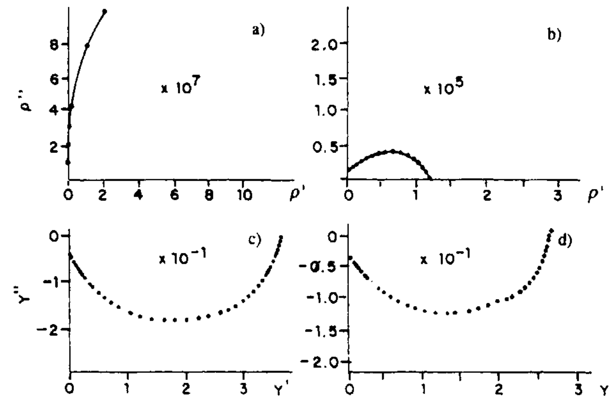


Figure 3 Impedance (ρ) and admittance (Y) arcs at 298 K of CB-filled systems with a ratio PVDF/PS 50/50 and different CB concentrations ($\%\phi_v$): (a) 2; (b) 10; (c) 30; (d) 38.

The electrical response of the system PVDF/PS/YBaCuO constitutes quite a different case. Complex

Table II Electrical Properties of CB-filled Systems

Composition % ϕ_v				
PVDF/PS	CB	σ (S cm^{-1})	ϵ' $\omega = 10^5$ Hz	tan δ $\omega = 10^5$ Hz
100/0	2	1.773 E-09	13.9	0.041
	10	1.960 E-03	802.5	68.0
	30	4.000 E-02	—	—
	35	4.180 E-03	—	—
70/30	2	6.402 E-10	10.3	0.037
	10	3.454 E-06	112.4	1.0
	30	7.100 E-03	—	—
	33	5.180 E-02	—	—
50/50	2	2.940 E-09	8.4	0.022
	10	8.478 E-06	107.0	1.9
	30	4.720 E-02	—	—
	38	3.280 E-02	—	—
30/70	2	4.664 E-10	6.2	0.009
	10	2.045 E-09	13.1	0.008
	30	8.560 E-02	—	—
	38	3.300 E-02	—	—

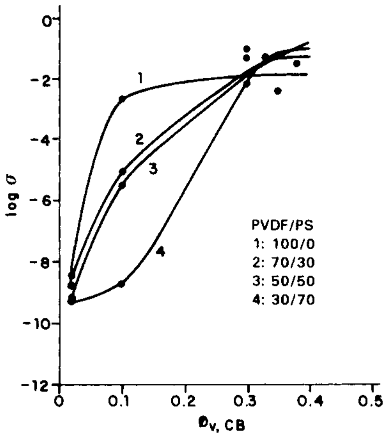


Figure 4 ϵ', tan δ, and σ as a function of CB content for PVDF/PS/CB systems.

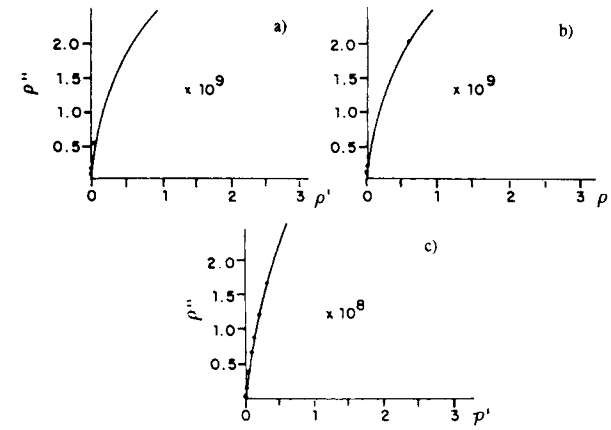


Figure 5 Impedance arcs at 298 K of YBaCuO-filled systems with a ratio PVDF/PS 70/30 and different YBaCuO concentrations (%ϕ_v): (a) 2; (b) 10; (c) 35.

impedance spectroscopy showed arcs as represented in Figure 5. As can be seen from the figure, these arcs are not "closed" and, hence, at first sight, are indicative of basically insulating materials, which was confirmed by the conductivity data, the dielectric constant, and tan δ compiled in Table III. The plot of these variables as a function of YBaCuO concentration is shown in Figure 6. Only slight variations are stated as a function of ceramic content (the dielectric constant, as well as the loss tangent, increase with YBaCuO concentration) and of the composition of the polymeric blend (the dielectric constant and the loss tangent decrease inversely proportionate to PS content for one and the same YBaCuO portion). Therefore, these materials refer to an equivalent circuit consisting of a resistor and a capacitor placed in parallel on the impedance (ρ) plane and very high R and C values.

The explanation as to why a superconducting ceramic with excellent conductive properties at ambient temperature should present conductivity values which are close to those of insulating materials when incorporated as a component into a polymeric system must be sought in the interaction mechanism with this system and more concretely in the aspect of "wettability," which governs particle crosslinking. This circumstance prevents any percolative conduction mechanism and even any tunneling effect from becoming active.

Table III Electrical Properties of YBaCuO-filled Systems

Composition % ϕ_v				
PVDF/PS	YBaCuO	σ (S cm^{-1})	ϵ' $w_2 = 10^5$	tan δ $w_2 = 10^5$
100/0	2	2.261 E-09	11.8	0.040
	10	5.138 E-10	13.0	0.044
	40	2.871 E-10	39.4	0.106
70/30	2	1.273 E-10	8.3	0.025
	10	1.212 E-10	12.7	0.040
	35	4.019 E-10	42.0	0.106
50/50	2	4.375 E-10	7.0	0.015
	10	1.293 E-10	9.6	0.024
	35	3.930 E-10	36.2	0.124
30/70	2	5.979 E-10	7.0	0.011
	10	1.183 E-10	7.7	0.013
	35	2.449 E-10	24.9	0.071

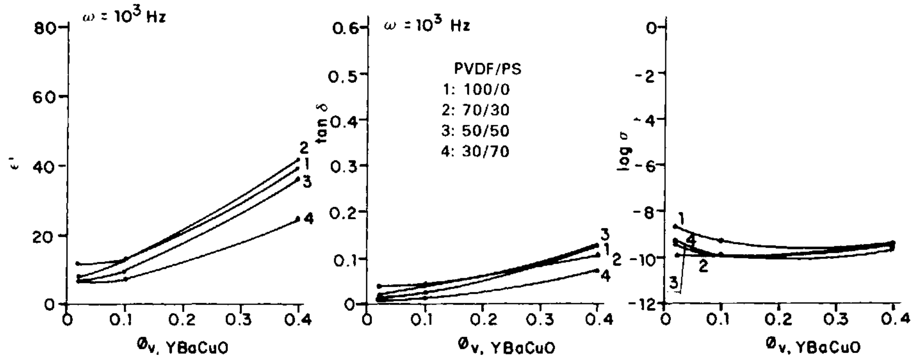


Figure 6 ϵ', tan δ, and σ as a function of YBaCuO content for PVDF/PS/YB systems.

Hence, all the samples, independent of YBaCuO concentration, are insulating from a conductivity point of view.

In the light of these results, it is reasonable to suggest that, on the one hand, the electrical characteristics of PVDF/PS/filler systems are strongly influenced by the nature and the content of the filler added to the polymeric blend and, on the other hand, that the influence of the polymer blend composition on the conductivity values obtained is almost negligible, except in the case of CB composites where at higher PS contents the conductivity diminishes for one and the same CB concentration.

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