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Conductivity study on semicrystalline and amorphous polymers filled with conducting additives

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SUMMARY

Polymeric conducting composites were obtained on the basis of polypropylene and polystyrene and conducting fillers (iron, copper and carbon black). The materials obtained by means of physical blends of the components were characterized through complex impedance diagrams. The respective data provided evidence of the fact that the conduction mechanism of such composites depends both on the chemical and structural properties of the polymeric matrix and on the nature of the conducting additive.

INTRODUCTION

The polymer in conductor composite systems containing metallic fillers is not limited to the exclusive role of acting as an inert agglomerant. On the contrary, its nature and properties play an essential part in the conduction mechanism, as well as in conductivity itself.

At present three physical processes, which govern and control electric charge transport in a conductor-filled polymer, are known (1): Percolation, tunneling and thermal expansion, i.e. mechanisms which are closely related both to the spatial arrangement of the conductor particles within the matrix and to the chemical, physical and structural characteristics of the polymer. In addition there exist three parameters (2) which affect directly the conductivity of the composites. First is the intrinsic conductivity of the additive, the greater additive conductivity, the higher the conductivity attainable in the composite. The second factor refers to the size and form of the additive; in terms of percolation and for the same additive concentration, the greatest number of contacts among particles is achieved with fribillar fillers. The third parameter is the filler wettability by the matrix, a feature which depends on the surface tension of the polymer (3), as well as on the specific interaction involved when contact is established between filler and a polymer.

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In the present study, the effect on conductivity of several conductor additives, when incorporated into different polymeric matrices is examinded, taking into account chemical, physical and structural characteristics of the polymer. Impedance plane complex techniques were applied to study polymeric composite obtained by introduction of iron, copper and carbon black into two conventional polymers, one is olefinic and semicrystalline (polypropylene) and another aromatic and amorphous (polystyrene).

EXPERIMENTAL

The following materials were used: POLYSTYROL 143 E from BASF, polypropylene ISPLEN powdered iron (10 μm) from Merck, powdered copper (63 μm) from Merck and ISAF carbon black (20 nm) from Cabot Laboratories.

The additives were incorporated in the molten state into the polymers in a Brabender type torque rheometer. Torque rate was set at 60 rpm, and chamber temperature was 200°C. The blends were retained in the mixing chamber for 10-12 minutes, i.e. the time necessary to achieve a homogeneous blend.

The electric characteristics of all components were determined with a 4162A LF Impedance Analyzer in the frequency range between 5 Hz and 13 MHz at room temperature.

RESULTS AND DISCUSSION

Tables 1 and 2 compile both the compositions and dielectric constants (at 10 Hz) as well as the conductivity values of the polystyrene and polypropylene families obtained. Carbon black concentrations above 30% in volume prevent to form stable composites, neither with polyproylene nor with polystyrene.

Figure 1 shows the dependence of conductivity on the aditive fraction of the each composite family. First af all, in the range of experimental concentrations polypropylene composites are comparatively better conductors than those of polystyrene-based materials, except for polystyrene-cooper composites at high filler concentrations. It is indicating that the percolation threshold is not rapidly reached by a polymer at a given filler concentration, because the wettability (which is related to the polymer surface tension of the filler by the polymer matrix plays an important role. High polymer surface tensions tend to decrease wettability (3) and hence to lower conductivity (e.g. Polystyrene, γ=43 dyne/cm) as compared to other polymers with a lower surface tension (such as polypropylene γ=32 dyne/cm). The conductivity value found for polysterene composite at the highest copper concentration, is abnormally high if compared to respecitve polypropylene values and, it is likely attributable to the fact that the unsaturated nature of the polystyrene favours the tunneling effect and hence significantly reduces the percolation threshold.

TABLE 1.- Compositions, dielectric constants and electric conductivities of the polystyrene composites

Sample	Composition, Φ_V				ϵ (10^4Hz)	σ (s . cm^{-1})
	PS	Fe	Cu	N		
SF5	0.80	0.20	-	-	40	$3,4 \times 10^{-7}$
SF6	0.70	0.30	-	-	696	$3,6 \times 10^{-3}$
SF7	0.60	0.40	-	-	1.000	$1,7 \times 10^{-3}$
SC5	0.80	-	0.20	-	67	$1,4 \times 10^{-5}$
SC6	0.70	-	0.30	-	118	$1,2 \times 10^{-4}$
SC7	0.60	-	0.40	-	206.000	$8,4 \times 10^{-1}$
SN3	0.90	-	-	0.10	942	$5,2 \times 10^{-3}$
SN5	0.80	-	-	0.20	1.236	$2,0 \times 10^{-2}$
SN6	0.70	-	-	0.30	-	0.153*

* Induction

TABLE 2.- Compositions, dielectric constants and electric conductivities of the polypropylene composites.

Sample	Composition, Φ_V				ϵ (10^4Hz)	σ (s . cm^{-1})
	PP	Fe	Cu	N		
PF5	0.80	0.20	-	-	35	$< 10^{-9}$
PF6	0.70	0.30	-	-	246	$3,1 \times 10^{-6}$
PF7	0.60	0.40	-	-	2.700	$2,3 \times 10^{-4}$
PC5	0.80	-	0.20	-	60	$1,0 \times 10^{-7}$
PC6	0.70	-	0.30	-	300	$3,3 \times 10^{-6}$
PC7	0.60	-	0.40	-	400	$1,3 \times 10^{-5}$
PN5	0.80	-	-	0.20	-	0.35**
PN6	0.70	-	-	0.30	-	0.62**

**Induction

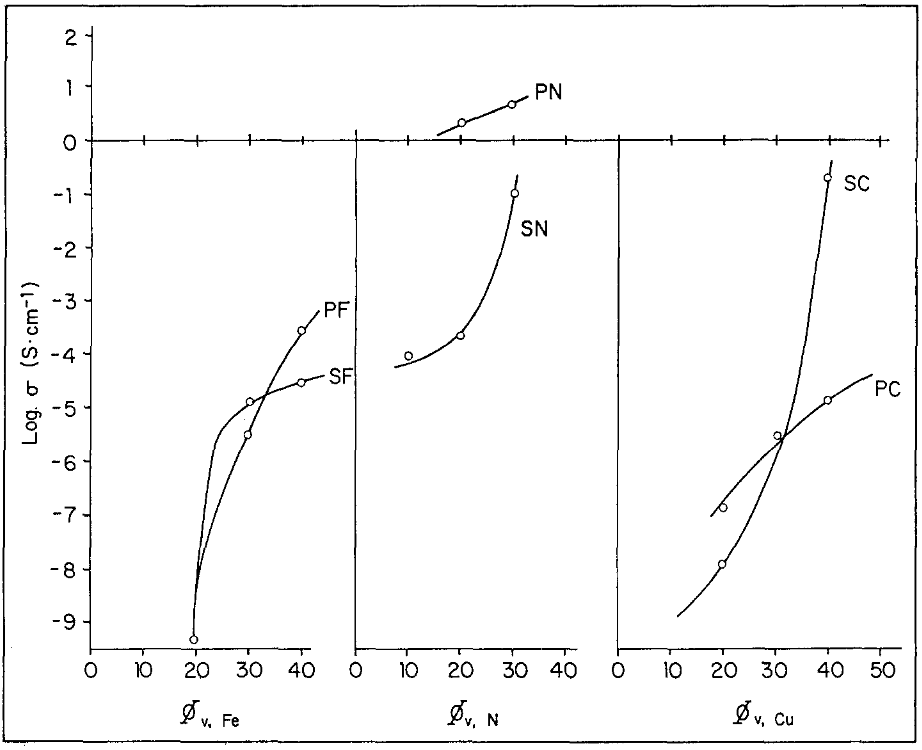

Figure 1. Variation of log conductivity as a function of volume content of filler for Iron (PF and SF) , carbon black, polypropylene (p) and polystyrene (S) composites.

Secondly, in any of the composites studied, conductivity increases as a function of additive concentration. The highest conductivity value coincided with the highest conducting filler concentration, which for iron and copper composites was 40% volume and in the case of carbon black 30% volume. At these concentration some components have not yet reached the total percolation, since above that concentration the composites is not possible to achieve stable material.

Thirdly, the conductivity values of composites obtained follows the serie: carbon black > copper > iron.

Finally, composites filled with carbon black, both in polystyrene and polypropylene matrix, showed electrical induction. Polystyrene exhibits electrical induction above 30% volume of carbon black and polypropylene just with 20% volume. The dependence of conductivity against frequency is showed in Figure 2 for samples exhibiting electrical induction. This figure shows again that polypropylene composites achieved

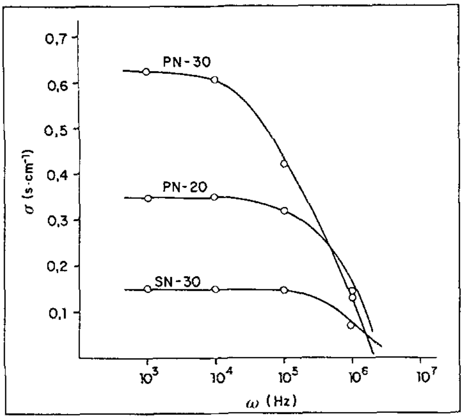

Figure 2. Variation of the conductivity as a function of frequency for the mentioned composites.

better conductivity behaviour than polystyrene at any frequency and for the same filler portion.

In the complex impedance analysis of iron and copper composites in polystyrene and polypropylene matrix a semicircle Argand (Cole-Cole) representation are observed. Material presenting such as arcs can be associated to an equivalen circuit formed by a resistance (R) and a capacitance (C). In addition such materials should possess polymeric interfaces among conductor partides (i.e. percolation has not taken place). Hence electronic conduction through the material is achieved by tunneling effect, in this case the composite behave like a semiconductor; that behaviour is also observed for carbon black-composites with no percolation at all.

The polypropylene and polystyrene-carbon black composites, when percolation is attained, behave in a similar way like an equivalent circuit (as inferred from their complex impedance diagrams) consisting of a resistance (R) in parallel to an inductance (L). That, in turn, is indicative of the fact that, for the filler levels studied, all additive particles have been interconnected (percolation) and thus a metallic type conduction has been achieved, free of dielectric interfaces among the particles.

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