Preparation and characterization of silver-filled polyester matrix composites

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In recent years there has been a steady increase in the use of plastic materials. Nevertheless, there are still some fields in which their properties could be improved or modified. One example is the insulating properties of polymers, which exclude them from applications requiring electric conductivity.

The aim of this study was to develop and characterize conductive composites with a polyester resin matrix.

Electrical resistivity can be decreased by the dispersion of conductive filler in the polymer [1]. Electrical conductivity in non-homogeneous conductors, such as composites containing conductive and non-conductive phases, is explained by the percolation theory [2]. In composites of this kind a percolation threshold is reached when the concentration of conductive filler dispersed in the insulating matrix is high enough to allow sufficient particle–particle contact to guarantee percolation of electrical conductivity.

Selection of conductive fillers is a complex task due to the number of parameters associated with the final properties of the composites, e.g. good mechanical properties and satisfactory mixing of filler and matrix, which normally exhibit low electrical resistance.

The first option, considering their low electrical resistivity, is to use a metal such as silver or copper. However, copper is inappropriate due to its surface oxidation and tendency to induce polymer degradation [3]. On the other hand, use of silver powder requires a reduced and homogeneous particle size in order to achieve optimal dispersion in the polymer matrix.

In this study, silver powder was prepared by reducing $AgNO_3$ with a diluted aqueous solution of hydrazine (NH_2NH_2), addition of a dispersion agent, and magnetic stirring for 6 hr. The resulting powder had a homogeneous particle size distribution, measured with a Beckman Coulter LS, showing, in the volumetric distribution, a d_{50} value of 13.5 μm and a d_{90} value of 23.6 μm.

An unsaturated polyester resin in 30–40% styrene was used as a polymer matrix. The resin was cured at room temperature, with addition of methylethylketone peroxide (MEKP) as initiator, and cobalt octanoate (12%) as a catalyst, until the gel point was reached. Styrene provided the cross-links between the polyester chains to form a thermoset polymer. Afterwards, the samples were heated in an oven at 80 °C to complete the curing process.

Composites were prepared by addition of the desired amount of silver and resin with the appropriate proportions of initiator and catalyst, 0.8 ml and 0.1 ml per 100 ml of resin respectively. These amounts are higher than those required to cure raw thermoset resin, because of the decrease in available peroxide due to a redox reaction with the metal.

We also studied the effect of addition of methylmethacrylate (MMA), another monomer containing carbon–carbon double bonds, in the development of the composites. MMA was added at 2–3% (v/v) in some of the mixtures, transferred to a cylindrical mould and then the mixture was slowly shaken until the gel point was reached, and cured in a furnace. The presence of this monomer during the mixing of filler and polymer matrix improved blending due to a decrease in the viscosity of the mixture.

Table I shows the characteristics of the silver and unsaturated polyester (UP) composites that were prepared.

Thermoset polyester was filled at levels of up to 75% (w/w), above this value samples showed cavities and fissures (see Fig. 1).

All samples had the same geometry (cylinders 15 mm high and 10 mm in diameter), and were characterized with a Metra Hit 16s tester. The contacts between the device and the sample were optimized by distributing a colloidal silver layer over the surface of the samples.

The electrical resistance of these composites corresponds to insulating materials. These high values indicate the presence of metal particles coated with an insulating polymer layer, which hinders electrical percolation through the composite. In order to break this insulating layer and achieve good particle–particle contact, a 1500 V electrical discharge was applied through the samples. After this procedure, qualitative differences as well as variation in the measured resistance values, facilitated the classification of samples into two groups, according to the presence or absence of MMA.

Table II shows the electrical resistance values of samples prepared in the presence of MMA. Note that a different behaviour was observed as a function of Ag content. Above 37% (w/w) Ag, consecutive electrical

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TABLE I Characteristics of the silver-UP resin samples

Sample	%Ag (W / W)	MMA
1	50	Yes
2	37	Yes
3	30	Yes
4	45	Yes
5	38	No
6	32	No
7	41	No
8	75	Yes

Figure 1 Photo showing the cavities of a composite with 80 % (w/w) of silver.

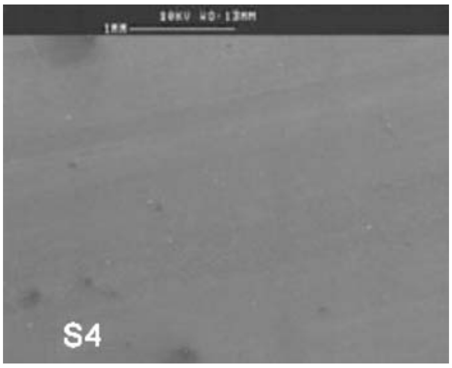

Figure 2 SEM micrograph of sample 4 prepared by addition of methylmethacrylate.

discharges had a considerable effect on the increase in conductivity.

In contrast, samples prepared without MMA (samples 5, 6, 7) showed electrical resistances higher than 50 MΩ even after electrical discharges, and showed higher tendency for damage by burning. This observation may be explained by the polarity of MMA causing an increase the adherence between silver and matrix, thus modifying the interface.

The morphology of the material was further studied by scanning electron microscopy (SEM). Fig. 2 shows the smooth surface of sample 4 prepared with MMA, whilst Fig. 3 shows that sample 6, prepared without MMA, has several holes in their surface. In Fig. 4 one of the cavities found in sample 5 is shown in detail.

TABLE II Samples prepared adding MMA (x%)

		Resistance (Ω)				
	% Ag (W/W)	Initial	1	2	3	4
1	50	65×10^6	380	95	15	15
2	37	60×10^6	2500	2500	2500	2500
3	30	6×10^6	6×10^6	6×10^6	6×10^6	6×10^6
4	45	50×10^6	10×10^6	42000	8000	40

Note. 1–4 refers to consecutive electric discharges.

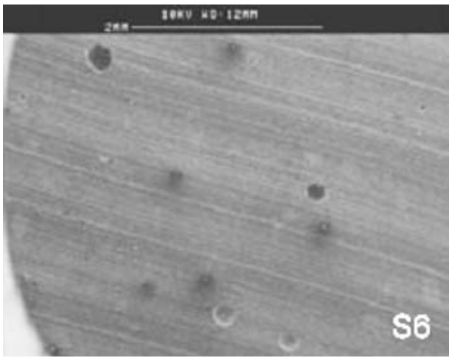

Figure 3 SEM micrograph of sample 6 prepared without MMA. Several holes are apparent on the surface of these samples.

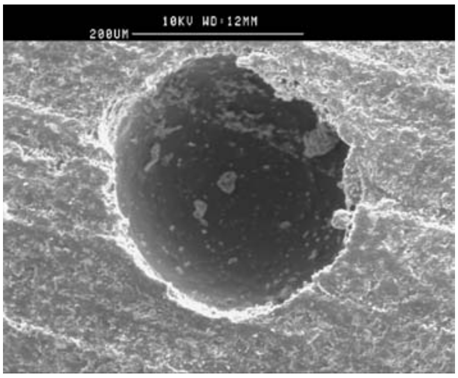

Figure 4 SEM micrograph showing in detail a hole observed in sample 5, a composite prepared without MMA.

Changes in resistance as a function of temperature were studied in samples 1 and 4, which had a higher initial electric conductivity. Individual samples were heated to different temperatures in an oven for 1 h. This treatment would be expected to cause a decrease in conductance, due to a loss of particle contact [4].

Thermosetting plastics do not exhibit such a pronounced thermal expansion as thermoplastics; polyester resin has a thermal expansion coefficient of $2.16 \times 10^{-5}/°C$ whereas the thermal expansion coefficient of silver is $18.7 \times 10^{-6}/°C$. Nevertheless, this difference is sufficient to result in an increase in the value of electrical resistance with temperature. Results are shown in Fig. 5.

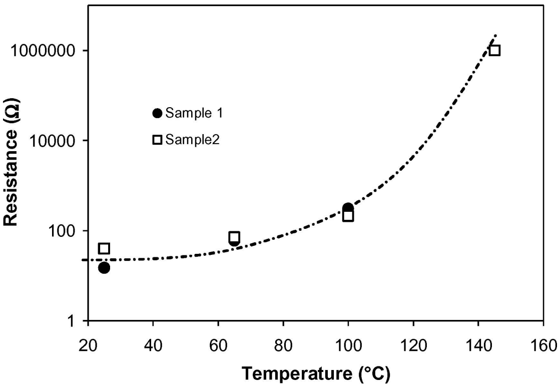

Figure 5 Increase in resistance values with temperature.

These results indicate that electrical resistivity strongly depends on temperature, the samples losing conductivity after glass transition (80 °C). It will be of interest to study this change in electrical behaviour further, especially its reversibility and the potential technological applications this could offer.

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References

1. W. JIA, R. TCHOUCAKOV, R. JOSEPH, M. NARKIS and A. SIEGMANN, *J. Appl. Polym. Sci.* **85** (2002) 1706.
2. S. KIRKPATRICK, *Rev. Mod. Phys.* **45** (1973) 574.
3. D. MARSHALL, *J. Adhes.* **74** (2000) 301.
4. N. C. DAS, T. K. CHAKI, D. KHASTGIR and A. CHAKRABORTY, *Polym. Polym. Compos.* **8**(6) (2000) 395.

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