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Low temperature magneto-conductivity properties of micro-sized Ag/HD-PE metal/polymers

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Abstract. A composite material of a polyethylene matrix filled by a fine silver powder was prepared with different Ag contents and physical behaviours ranging from insulator to conductor. Ac differential magnetic susceptibility χ measurements show the samples are paramagnetic up to an Ag concentration of ∼65%. At low temperatures the composite is spin-glass type, whereas the transition from insulator to conductor corresponds to an abatement of χ at zero magnetizing field. Magneto-conductivity effects have been observed in resistivity measurements at low temperatures. They can be explained in terms of an effective exchange electronic scattering mechanism between the conduction electrons and the diluted magnetic moments arising from unpaired electron spins of boundary silver particles. Moreover, the presence of a broad minimum in the resistivity curve at $T =\sim 20$ K, observed in samples with an Ag concentration just above the percolation threshold, addresses to possible interference effects similar to those reported in disordered materials.

PACS. 72.80.-r Conductivity of specific materials – 72.80.Le Polymers; organic compounds (including organic semiconductors) – 81.05.Lg Polymers and plastics; rubber; synthetic and natural fibers; organometallic and organic materials

1 Introduction

Electrically conductive polymer composites, consisting of a metallic filler and an insulating polymer matrix, play an important role in the field of advanced functional composite materials owing to their advantages in terms of light weight, chemical stability, cost effectiveness, easy control of both electrical and mechanical properties over a wide range. In recent years there has been a renewed interest for such composite metallic materials for their interesting magnetic properties [1–3]. The reason of this renewed interest has to be found in the possibility they offer to show well defined electrical and/or magnetic properties activated by an external stimuli. The possibility to use them as intelligent sensors, *i.e.* sensors able to response to an external signal and at the same to control it by means of an intrinsic negative feedback, also justifies the interest of the scientific community around this class of materials. Moreover, measurements of magnetic and electrical properties of such composites at low temperatures are a powerful tool to investigate different theories on disordered magnetism above all in reduced size systems.

This paper presents experimental results concerning with electrical and magnetic properties of a polymer-metal composite (silver/polyethilene, Ag/HD-PE). In particular, Section 2 describes the synthesis of the Ag/HD-PE composite together with a complete characterization in terms of structural properties. In Section 3 measurements of both transport and magnetic properties as a function of temperature are presented for different Ag concentrations, ranging from the insulating to the conducting regime, and for different magnetizing field levels. The discussion of experimental results is presented in Section 4 according to general theories on disordered magnetism.

2 Experimental

2.1 Preparation

The investigated material was a polymer-based microcomposite obtained embedding a micrometric powder of pure silver into a continuum polyethylene matrix. In particular, a 2–3 μm silver powder (Aldrich Chemical, 99.99%) and high density polyethylene (HD-PE, Aldrich Chemical, $Mw = 100\,000$) were used without any purification to prepare the composite material. Samples were obtained by mixing the silver powder with the molten polyethylene using a stainless steel spatula and a low power hot-plate surface (to avoid the thermal degradation of the molten

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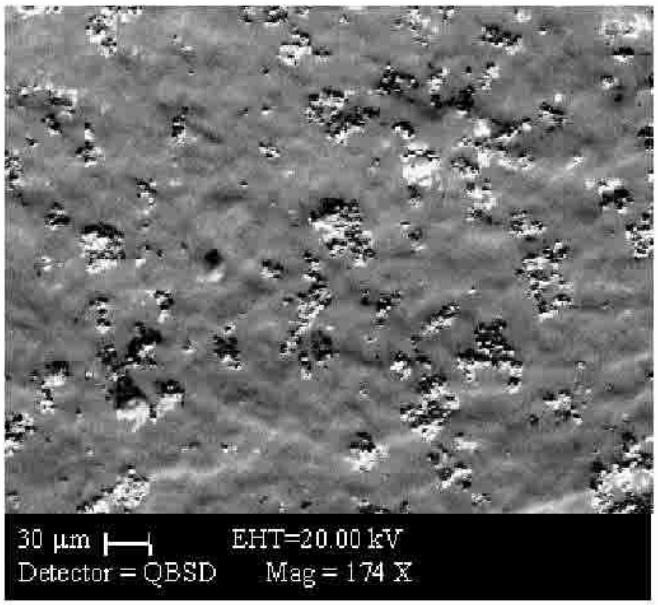

Fig. 1. SEM microphotograph of a 55% Ag fabricated composite. The picture clearly shows the particles are totally embedded in the polymeric matrix with a negligible microporosity.

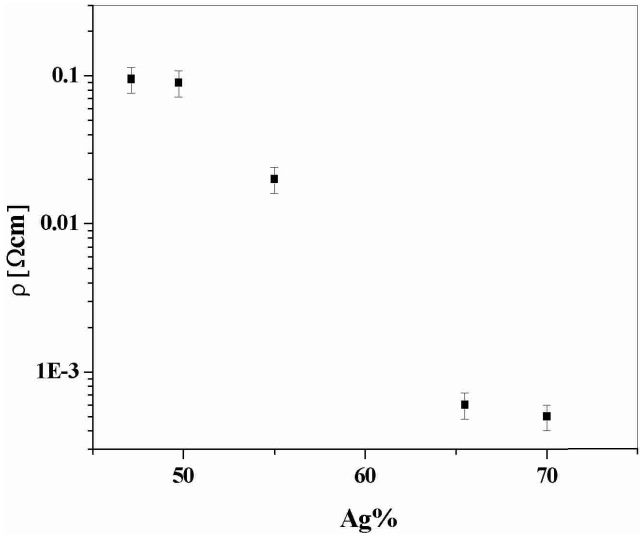

Fig. 2. Room temperature resistivity *vs.* Ag percentage content for prepared samples.

polymer). An Al foil was placed on the hot surface to facilitate the removal of samples after mixing. Uniform composite films with a thickness of about 2 mm were obtained by a hot-isostatic press. The material composition was determined by thermo-gravimetric analysis (TGA, DuPont) working in a nitrogen atmosphere. Silver particle morphology, average size, and composite microstructure were obtained by scanning electron microscopy (SEM, LEO Cambridge-440). The EDS analysis was performed with a Link-AN 10000 apparatus working on a Cambridge-240 SEM microscope. From the microscopic analysis of the powder structure it resulted that a number of submicrometric spherical particles were sintered together to give agglomerates with a mean size ranging from 1 μm to 20 μm. The microstructure of a sample corresponding to an Ag concentration of 65% is shown in Figure 1. The particles are totally embedded in the polymeric matrix and there is just a negligible microporosity. EDS analysis excludes the presence of spurious magnetic particles resulting from the compounding process.

2.2 Resistivity measurements

Resistivity measurements on Ag/HD-PE samples with different Ag concentrations were made by using a standard four probe technique with an in line equal spacing probe configuration. Room temperature d.c. resistance measurements were done by using a standard Van der Paw system with spring-loaded tip contacts. The used current was kept below 10 μA. The use of such a low current means that the noise in the resistance measurement was a a few parts in 10^5. Low temperature measurements were performed in a standard super-insulated helium cryostat operating in the range 4.2 K–300 K. Electrical contacts were obtained by using silver paint. Because of the samples are complex networks of chains of Ag particles, it is likely that the chains could not support higher currents because of the Joule heating effect. Ac synchronously demodulated resistance measurements were also performed in order to test the ohmic nature of currents by monitoring continuously the output signal phase. According to reference [4], for equally spaced leads the resistivity can be calculated from the knowledge of the current I through the sample and the voltage V between inner contacts by using the equation $\rho = 2\pi S\left(\frac{V}{I}\right)$, where $S = 1$ mm is the spacing between leads. Figure 2 shows the room temperature resistivity of prepared composites as a function of Ag concentration, with the error bars displaying the σ-spread of all tested samples corresponding to the same metallic concentration.

In Figure 3 resistivity *vs.* temperature curves are plotted for samples with Ag concentrations just above, *i.e.* Ag% of 55 (see Fig. 3a), and above, *i.e.* Ag% of 65 (see Fig. 3b), the "critical concentration", *i.e.* the concentration corresponding to the formation of a conducting path inside the composite. For both of them the curve corresponding to the application of an external magnetic field $H = 160$ kA/m, parallel to the current flow direction, is also showed. In Figure 4 the difference between the resistivity with (ρ_H) and without ($\rho_{H=0}$) the magnetic field as a function of temperature is reported for the sample with an Ag concentration of 55%. Data are normalized to the room temperature value $\rho_{H=0}(300\ \mathrm{K})$. No significative features were observed within the experimental errors for samples with larger Ag concentrations.

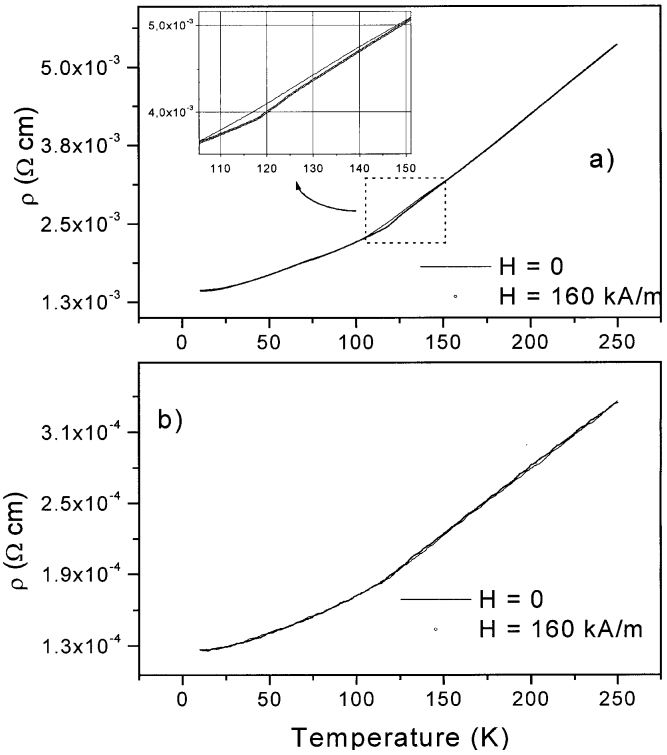

Fig. 3. Resistivity *vs.* temperature plots for samples with Ag concentrations (a) just above (55% Ag)) and (b) well above (70 Ag%) the critical concentration at two different values of the applied magnetic field.

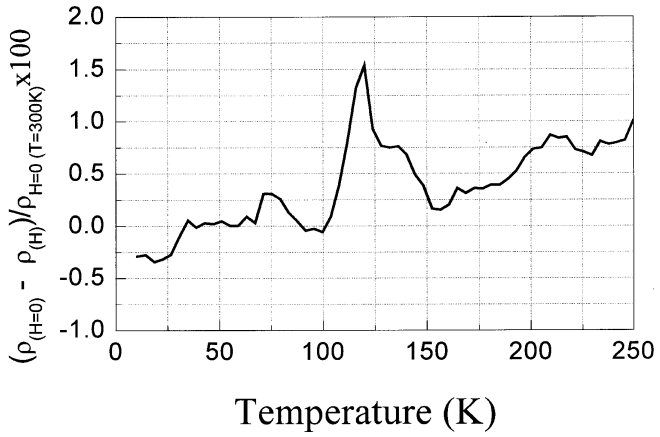

Fig. 4. Normalized resistivity change due to the application of the magnetic field as a function of temperature for the sample with an Ag concentration of 55%. Data are normalized to the room temperature value $\rho_{H=0}(300\ \mathrm{K})$.

2.3 Magnetic measurements

The differential magnetic susceptibility of the composite as a function of the temperature was measured by means of an AC Susceptometer (Oxford Instrument). Susceptibility *vs.* temperature data for Ag/HD-PE samples containing different silver contents are presented in Figure 5. The measurements were performed at a fixed field intensity of 160 kA/m where the maximum ac susceptibility (1000 Hz) at room temperature was obtained. Some clear cusps extruded from a paramagnetic background occurs; the main ones are observed at about 120 K, 60 K and 25 K respectively. The cusp at 120 K is mainly prominent for the sample with an Ag concentration of 30% and becomes more smeared in other samples. On the other hand, a large concentration of Ag particles (>67%) produces a strong decrease of the magnetic susceptibility, which tends to a behaviour typical for bulk silver.

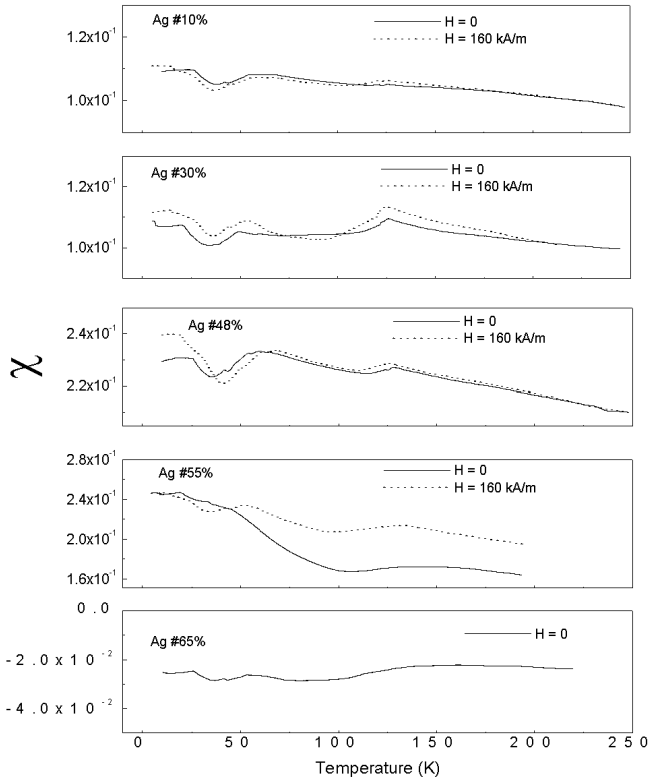

Fig. 5. Ac differential magnetic susceptibility *vs.* temperature for Ag/HD-PE samples with different silver percentage contents.

3 Discussion

The paramagnetic behaviour of the investigated metal-filled composite shown in Figure 5 has been already observed and explained in terms of unpaired electron spins at the boundary of silver particles [5,6]. The slight increase of the magnetic susceptibility χ with the Ag percentage is related to the increasing presence of unpaired spins, since an increment of the agglomerates' number is consequently expected. When metal particles physically contact themselves, the number of unpaired electrons on the free boundary surface decreases as the magnetic susceptibility χ. The abundance of Ag produces a strong decrease of χ at zero magnetizing field when the bulk properties of Ag dominate. In the non-conductive composite (*i.e.* Ag%

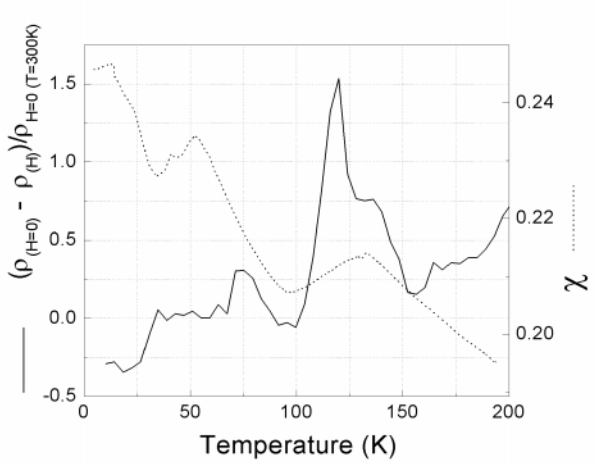

Fig. 6. A comparison between the a.c. differential magnetic susceptibility $\chi(H = 160$ kA/m) and the normalized change in the resistivity, *i.e.* $(\rho_{H=0} - \rho_H)/\rho_{H=0}(300$ K) in the sample with a 55% percentage of Ag.

$< 48\%$) the χ curve at zero field and at 160 kA/m respectively are almost coincident. On the other hand, when a conducting network has been established, the zero field curve is below that corresponding to the application of the external field. In this condition the boundary unpaired electrons became conduction electrons so that, since magnetic atomic moments depend on their spin, the magnetic interaction among the nearest boundary atoms, which determines a magnetic susceptibility at zero field, noteworthy decreases.

The resistivity measurements clearly show the existence of correlations between transport and magnetic properties. While at high temperatures the behavior of $\rho(T)$ reflects the almost metallic trend expected for Ag particles embedded in the polymeric matrix, the situation is quite different in the low temperature range ($T < 150$ K), where a well defined deviation from the linear temperature dependence is observed. In a previous publication [7], authors fitted data in this region with a $\rho(T) \sim T^2$ dependence addressing to some non-phononic spin scattering mechanism limiting the electron lifetime [8]. The presence of a correlation between peaks in the magnetic susceptibility χ and the normalized change in the resistivity, *i.e.* $(\rho_{H=0} - \rho_H)/\rho_{H=0}(300$ K), in a sample with 55% percentage of Ag, is unambiguously demonstrated by data reported in Figure 6. The effective electron scattering mechanism, which is dominant over the electron-phonon coupling at low temperatures, is also responsible for the resistivity decrease in resistivity following the application of the external magnetic field. The presence of negative extra contribute to resistivity has been previously observed in alloys of transition metals or rare-earth elements containing magnetic ions [9] or in amorphous alloys [10]. Different explanations have been proposed to explain the origin of this contribute, ranging from spin-flip scattering in crystalline alloys exhibiting the Kondo effect to the scattering from two level structural excitations; nevertheless, but none of them completely describes the observed phenomenology. In the investigated Ag/HD-PE metal polymer composite the role of magnetic ions could be played by disordered local moments arising from super-paramagnetic micro-sized Ag clusters dispersed within the polymer matrix. In fact, when the metal is reduced to a micro-sized powder finely dispersed into a non-magnetic matrix, and hence no agglomeration is present, the resulting material shows paramagnetic properties (see Fig. 5). The change of the magnetic properties in Ag is due to the probability for the fine particles to result in a net unpaired spin due to an odd number of electrons. In fact, particles with an odd number of electrons are expected to exhibit a magnetic moment and hence a spin-glass type behavior [5]. At low temperatures, the particles with an odd number of electrons are frozen in a disordered state, while at higher temperatures the spin orientations are governed by magnetic exchange interactions which over-crosses thermal fluctuations. Consequently, the magnetic susceptibility of a composite containing these silver particles exhibits significant cusps at temperatures sharply defined, thus suggesting a second order phase transition from a super-paramagnetic state to a local spontaneous paramagnetic-type magnetization. The spin-glass type transition can be observed just for a narrow range of the Ag concentration near the insulator-conductor transition because the metal content must be sufficiently high to allow short-range interactions among the magnetic moments but low enough to avoid the coalescence of particles with an odd number of electrons resulting in a diamagnetic behavior. The interaction between the conduction electrons and the disordered local magnetic moments arising from unpaired spins of Ag particles can influence transport properties as observed in resistivity curves shown in Figures 3 and 4 respectively.

Moreover, data of Figure 6 show also an inversion of the sign for the normalized change of the resistivity around $T = 20$ K where the condition $\rho_{H=0}(T) < \rho_{H\neq 0}(T)$ is achieved. Even if measurements can not be considered conclusive looking at this feature, this structure deserves some further considerations since it could be a signature of a different electronic coupling mechanism. We found clear analogies with similar effects predicted by Fert theory [11] based on exchange scattering. In particular, the magnetic contribute $\rho_{\rm m}$, which adds to the phononic and the impurity terms respectively in the Mathiessen rule, contains two terms depending on the concentration of the dilute magnetic moments c, *i.e.* $\rho_{\rm m} \cong \rho_{sd}\{c + c^2[S_{AA}(2k_{\rm F}) - 1]\mu^2\}$, where μ and S_{AA} are the local magnetization factor and the partial structure factor respectively [12]. The two terms are due to the scattering by individual magnetic moments and to electronic interference effects respectively. The last term acts in a manner analogous to the Faber-Ziman theory [13,14]. As a consequence, the whole sign of $\rho_{\rm m}$ depends on the interference term $S_{AA}(2k_{\rm F}) - 1$, which can be positive or negative according to whether the partial structure factor S_{AA} is greater or less than 1. Effective positive interference contributions arising from diluted unpaired spins

moving in electron closed loops along the main network can be responsible for the presence of the above mentioned feature at $T \leq 20$ K as evidenced in Figure 6. These loops can arise from the metallic coating realized over the micro-sized polymer spherulites. Similar effects have been recently observed in low temperature magnetoresistance measurements on nanostructured Ag [15]. However, further investigations are needed in order to understand completely the physical origin of this sign inversion in the magnetoresistance of micro-sized metal filled composites.

4 Conclusions

In conclusion, transport and magnetic properties of a metal/polymer composite material formed by μ-sized Ag particles and high density polyethylene (Ag/HD-PE) have been extensively studied for different Ag concentrations. The whole range from a pure insulating to a full conducting regime of the resulting plastic has been investigated. Interesting and anomalous properties occur at low temperatures both in resistivity and ac differential magnetic susceptibility measurements. In particular, well defined cusp-like peaks at $T = 120$ K and $T = 60$ K are present in the magnetic susceptibility curves. They depend on the freezing of spins resulting from a super-paramagnetic behaviour of unpaired electrons in μ-sized Ag clusters. Such a behaviour is destroyed by high contents of silver particles (>65%), showing in this limit the magnetic properties of bulk Ag. A clear correlation between these peaks and the electron transport properties has been evidenced. In particular, when some conducting network appears, an increase in the material conductivity is observed when an external magnetic field is applied. The negative magneto-resistance effect observed at low temperatures has been explained as a result of the interaction between the conduction electrons and the disordered local magnetic moments arising from unpaired spins of Ag particles. Moreover, an additional feature in the magnetoresistance at lower temperatures ($T \leq 20$ K) has been also observed for samples with an Ag content close to the critical composition. Positive electronic interference effects occurring in the exchange magnetic scattering between conducting electrons and dilute magnetic moments of unpaired spins in μ-sized Ag/HD-PE agglomerate can qualitatively explain the experimental result, even if other measurements are needed for studying systematically this effect.

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