Polymer Bulletin 57, 881–887 (2006)
DOI 10.1007/s00289-006-0648-6

Polymer Bulletin

Electrical and magnetic properties of Polystyrene doped with Iron nanoparticles

L.C. Costa[a] (✉), M. Valente[a], M.A. Sá[b], F. Henry[c]

a) Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal
b) IFIMUP and Physics Department Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
c) Laboratoire de Recherche en Polymères, C. N. R. S., 94320 Thiais, France
E-mail: kady@fis.ua.pt

Received: 2 June 2006 / Revised version: 10 July 2006 / Accepted: 12 July 2006

Summary

Polymer composites have recently received a considerable amount of scientific and technological interest, because their properties can be properly controlled, choosing the adequate doped particles, their size and concentrations, and the synthesis conditions.
In this work we report the synthesis and characterization of a polystyrene (PS) matrix doped with different concentrations of iron nanoparticles.
X-ray diffraction and transmission electron microscopy were used to characterize the structure of the samples. The behaviour of the d.c. electrical conductivity (σ_{dc}) and the complex permittivity ($\varepsilon^* = \varepsilon' - i\,\varepsilon''$) as a function of frequency (100 Hz-10 MHz) reflects the important effect of the iron nanoparticles concentration in the sample properties. A percolation threshold in the conductivity was observed at a critical concentration of iron nanoparticles. A noticeable increase in the saturation magnetization and coercivity is observed with the rise of the iron nanoparticles concentration, being thisbehaviour also noticed in the remanent magnetization. A rise of the initial a.c. susceptibility with the iron concentration is also observed.

Introduction

The study of the structure, the properties and the dynamics of polymeric composite systems [1-4] is particularly important for the development of new materials for specific industrial applications. The applications of conducting polymers include the use as conducting wires, electromagnetic shielding materials [5,6], microwave absorbent [7], light emitting diodes [8], sensors [9], etc.
The electrical conductivity of an insulating polymer can be improved greatly by adding conducting particles like carbon [10-12], iron [13-15], nickel [16, 17] or another conducting polymer [18-20]. Generally, the conductivity of a polymer, rather than being a linear function of the concentration of the added particles, is almost insensitive for lower concentrations, and rises abruptly as the percolation threshold is reached [21]. This occurs at a critical concentration where the particles contact with each other and, as a consequence, a continuous electrical path of the doped particles is built throughout the polymer matrix. So, the properties of the composite material can be controlled by

properly choosing the components, their shape, dispersion state, relative concentrations and interactions.

Dielectric spectroscopy has proven very useful for studying the conformation, the structure and the dynamics of polymeric systems [22], and consequently the percolation behaviour can be observed by this technique [23]. The measured quantities, ε' and ε'', have a direct physical interpretation. The real part of the permittivity is related to the energy stored in the material and the imaginary part is proportional to the dissipated energy by cycle. So these quantities produce useful information regarding the electrical characterization of the material.

Nanophase materials often exhibit new phenomena and their physical properties are often different from their bulk structures. Below a critical size, magnetic particles become single domain as opposed to multidomain in the bulk structure. Polymer systems with nanoparticles of metal can be tailored to exhibit novel electrical, magnetic and optical properties.

Polystyrene (PS) is one of the most interesting polymers due to their novel properties: it is readily available and presents good environmental stability, easy processing, light weight and low cost.

In this work we report the synthesis of a polystyrene (PS) with iron nanoparticles. The electrical conductivity, the permittivity, the magnetic hysteresis cycles at 300K and the a.c. magnetic susceptibility as a function of temperature have been studied.

These kind of composites in which the matrix of polystyrene is non-reactive and protects the nano metal particles are likely to have a wide range of electric and magnetic applications.

Experimental

We produced polymer composites made of polystyrene (PS) particles and iron nanoparticles, in concentrations between 2% and 30% per weight. The aqueous emulsion polymerisation technique, in a concentration of 0.09 mol/l, gives monodispersed PS microparticles, used later as host matrix with conducting nanoparticles. The calculated molecular weight of PS was about 450000. Iron nanoparticles were synthesized by fusion of iron bars, in levitation, at cryogenic temperatures [24]. The powder, a mixture of PS microparticles and iron nanoparticles, is pressed in a molten at 50 MPa, at 110 ^{o}C, just above the glass transition temperature of the PS (100 ^{o}C), during 30 minutes. After pressing, the samples are allowed to cool freely to room temperature.

X-ray diffraction patterns were obtained at room temperature, in bulk samples, with a Rigaku XDMAX diffractometer (λ=1.5418 Å) at 40 kV, and 30 mA, with a step of 0.05° and a time per step of 1 s. The size and location of Fe particles were measured by transmission electron microscopy (TEM) on thinned samples mounted on a carbon-coated grid with an applied voltage of 100 kV. Since the material must be exposed to a very high vacuum when being examined, it was dried at a previous stage in its preparation.

For the electrical measurements, the samples were prepared as discs with 10 mm diameter and a thickness about 1 mm with aluminium electrodes on the opposite sides of the samples. Copper leads were bonded to the electrodes using silver paint. The electrical d.c. conductivity (σ_{dc}) measurements were made using a Keithley 617 programmable electrometer, at constant temperature 300 K in a helium atmosphere to improve the heat transfer and eliminate the moisture. The stabilisation of temperature was better than 0.1 K over the period of measurement of current. The electric field was applied in steps of 10 kVm^{-1}, the highest field being about 100 kVm^{-1}.

The impedance spectroscopy measurements were carried out at room temperature, in the frequency range 100 Hz -10 MHz using a Stanford Research Systems SR850 lock-in amplifier, in the typical lock-in configuration [25], measuring the 'in phase' and the 'out of phase' components of the output signal. These quantities are then used to calculate the values of effective resistance and capacitance in a parallel RC (Resistance-Capacitor) model of the sample.

The alternating current magnetic susceptibility (χ_{ac}) measurements, between 80 and 320 K, were done at 119.5 Hz in a magnetic field of 10 Gauss, using a home-built mutual inductance differential transformer system. The accuracy of temperature control and measurements was better than 0.1 K over the whole range and the overall accuracy of the measurements of the magnetic moment is better than 0.2%. The magnetic hysteresis cycles were measured at 300K using a Vibrating Sample Magnetometer (Oxford Instruments) with magnetic field ranging from -1T to 1T.

Results and Discussion

Particles of relatively uniform quasi-spherical shape, with approximately the same size, were observed in the TEM images. For lowers concentrations the samples show isolated particles and/or small groups of aligned particles. For concentrations of iron nanoparticles larger than 12 %, aligned particles were observed (figure1). These chain-like entities, of quasi-spherical iron nanoparticles, become more numerous with iron concentration. It is reasonable to assume that the overlapping of these structures would also grow, and their mutual interactions become stronger as the distance between them decreases, due to the increase of iron concentration. Transmission electron microscopy images show that the nanoparticles are distributed throughout the polystyrene matrix. The average size of the iron particles was calculated to be 145 nm, approximately.

Figure 2 presents a typical XRD spectrum of the samples with 6% and 30% of iron per weight. For comparison the spectra of pure polystyrene is also shown. XRD analysis indicate that in 30% sample is present metallic iron (Fe) and magnetite (Fe_3O_4) and the 6% sample shows only the Fe diffraction peaks. This analysis is in agreement with

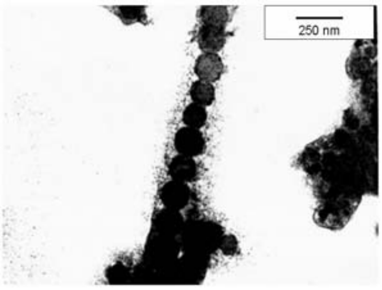

Fig. 1 - Transmission electron microscopy (TEM) image of the iron particles in the PS matrix.

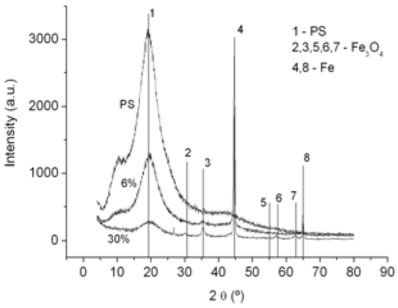

Fig. 2 - XRD spectra of the sample with 6 and 30% of iron by weight, and pure polystyrene.

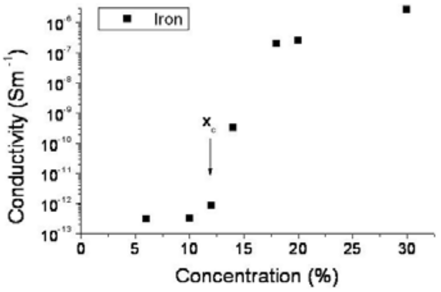

Fig. 3 - d.c. conductivity versus concentration of iron particles in the PS matrix, at T=300 K.

JCPDS Numbers (74-0748, 85-1410). The non detection, by XRD, of the Fe_3O_4 phase in the samples with small concentration of iron nanoparticles is probably due to their small sizes. The sharp peaks and their relative intensities observed in PS/Fe nanocomposites are nearly corresponding to those of Fe_3O_4 and Fe. This indicates that the crystalline structure of Fe_3O_4 and Fe is preserved and no obvious chemical interaction between these ions and the PS is observed.

Figure 3 shows the d.c. conductivity versus concentration of iron conducting particles in the PS matrix, at 300K. The conductivity of pure polystyrene was $1.5*10^{-13}$ Sm^{-1}. The existence of a critical concentration x_c, "percolation threshold", at which σ_{dc} begins to increase abruptly is visible. The percolation theory predicts that at a certain amount of concentration of particles a full conducting path is formed for the flow of current. This has also been confirmed from TEM, which shows the formation of complete chain pattern connecting the nanosized particles (figure 1). If chains-like paths are formed by metallic iron nanoparticles the expected conductivity would be much larger than the observed. So, the σ_{dc} data suggests that the particles have a Fe core covered with an insulating material, or that the iron nanoparticles are protected by the polymer matrix. The percolation threshold for 12% of iron particles concentration can be explained by the shape of the nanoparticles. It is expected that spheres in a matrix will create a higher critical concentration than that obtained with fibrous fillers [26]. The chemically inert helium atmosphere used during the conductivity measurements avoids moisture in the samples and guarantees that the conductivity changes are not due to any chemical reaction in the sample. The large difference between conductivities of iron particles and polystyrene promotes the appearance of defect charges in the interfaces, which are loosely bound. They are responsible for the conductivity at lower concentrations.

To obtain complementary information about the conductivity process, we measured the a.c. complex permittivity, in the frequency range 100 Hz to 10 MHz. The spectra of the real and imaginary parts, ε' and ε'', as a function of frequency, at constant temperature, T=300 K, for different concentrations of the iron nanoparticles, are shown in figures 4 and 5. It is not possible to determine the mean value of the relaxation time distribution of the composites because it is not observed a maximum in ε'' versus frequency (figure 5). The same is observed in the others plots usually used, M' versus M'' (modulus formalism) and Z′ versus Z'' (complex impedance formalism).

From these figures, it is observed that the values of ε' and ε'' are almost constant for concentrations of iron lesser than 12%. The increase of the dielectric constant with the rise of iron concentration can be ascribed to the increase in the volume fraction of the charges (electric dipoles) in the interfaces between Polystyrene (PS) and the iron nanoparticles. On the other hand, the increase of ε'', connected to the a.c. conductivity, may be due to the proximity between the iron nanoparticles. The large increase of ε'

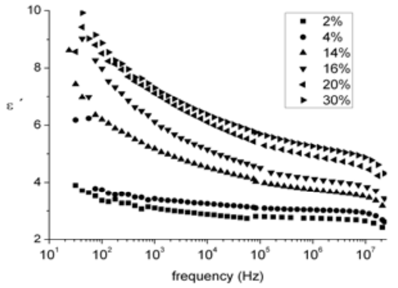

Fig. 4 - ε´ as a function of frequency, at constant temperature, T=300K.

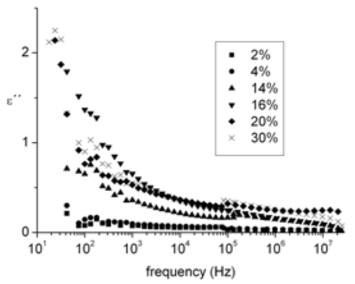

Fig. 5 - ε´´ as a function of frequency, at constant temperature, T=300K.

and ε´´, for concentrations of iron larger than 12%, can be related with the percolation threshold. In disordered materials, one would expect a variation in the free energy barriers from site to site in the quasi lattice, unlike in a material with a long range lattice structure. Ions under a low frequency electric field can hop readily out of sites with low free energy barriers but tend to 'pile up' at sites with high free energy barriers. This leads to a net polarization of the sample and to a large value of ε´. At high frequencies the polarization due to charge 'pile up' disappears and ε´ decreases [27]. This can explain the behaviour of the complex permittivity as a function of frequency.

Figure 6 presents the magnetic hysteresis cycles for the samples with 2% and 30% of iron, at room temperature. The 2% sample shows a small hysteresis loop. The magnetic response, hysteresis, coercivity and remanence increase with the particle concentration of iron. Remanence varies from 0.6 to 12 emu.g^{-1}, saturation from 3.2 to 46 emu.g^{-1}and coercivity from 0.005 to 0.05 T, when the concentration increases from 2% to 30%. These effects can be interpreted as being a consequence of an increasing anisotropy due to the formation of the chain-like entities and the increase of the Fe_3O_4 content. For the samples with the highest concentration of iron it is observed, by DRX, the presence of the Fe_3O_4 particles (magnetite) showing that we have oxidizing conditions in the samples. From these results we can admit that the nanoparticles are composed by a ferromagnetic Fe core with the ferrimagnetic Fe_3O_4 shell. Our data suggest that interparticle interactions affect the coercivity and the remanence of the samples.

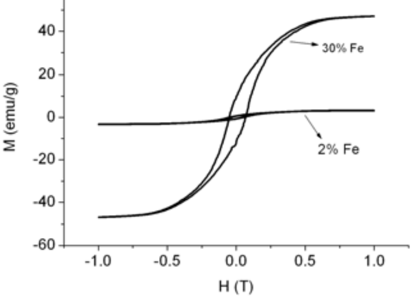

Fig. 6 - Magnetization for the samples with 2% and 30% of iron, at room temperature.

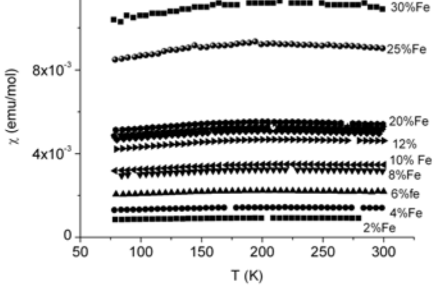

Fig. 7 - Temperature dependence of a.c. susceptibility. The applied a.c. magnetic field was 10 Oe.

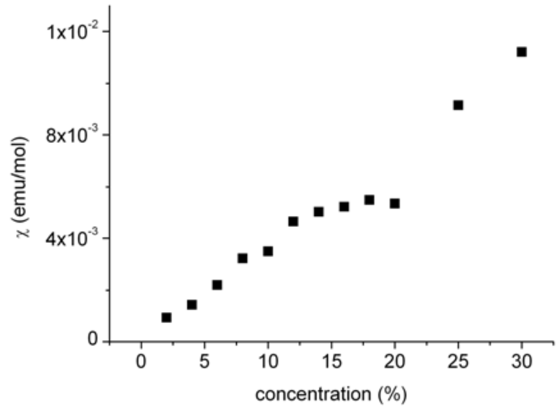

Fig. 8 - Concentration dependence of a.c. susceptibility, at T=250 K.

The temperature dependence of the a.c. magnetic susceptibility (χ_{ac}) presents a broad maximum at approximately 210 K (figure 7) for all the samples. It is found that the peak position of the a.c. susceptibility of the nanocomposites shifts to a higher temperature (≈210K) compared with that of pure Fe_3O_4 nanoparticles (190-200 K) [13].

It is, also, observed an increase of the magnetic susceptibility with the rise of the iron concentration (figure 8). However, for the samples with a concentration of iron between 10 and 18%, near the percolation threshold, the value of the susceptibility is almost constant. This behaviour can be ascribed to the interaction between the iron particles that are in the chains.

Conclusion

The large difference between conductivities of iron particles and polystyrene promotes the appearance of defect charges in the interface, which are loosely bound. They are responsible for the conductivity at lower concentrations. The conductivity data does not show much change for lower concentrations of iron. A marked increase in the conductivity is observed for a concentration of 12% of iron. For higher concentrations, the conducting process is dominated by the percolating paths, in parallel with other non percolating paths formed by isolated iron (Fe) and/or magnetite (Fe_3O_4). The enhancement of electrical dipoles with concentration explains the behaviour of dielectric constant.

The saturating magnetization of the samples depends on the volume fraction of the iron nanoparticles. The magnetic response, hysteresis, coercivity and remanence increase with the particle concentration of iron.

For the samples with a concentration of iron between 10 and 18%, near the percolation threshold, the value of the susceptibility is approximately constant.

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