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Piezoresistivity of magnetorheological elastomers

N Kchit and G Bossis

LPMC UMR-CNRS 6622, University of Nice Sophia Antipolis, 06108 Nice cedex 2, France

E-mail: bossis@unice.fr

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Abstract

Magnetorheological elastomers are smart materials made by aligning magnetic microparticles inside a liquid polymer before the curing process has started. Once cured, the composite presents new properties such as a large change of elasticity when applying a magnetic field. We analyze here another specific property of these materials which is the piezoresistivity. Two cases are studied: one where the particles inside the matrix are not in contact and the other where they are in contact. We show that in the first case we observe an exponential dependence of the resistivity versus pressure and in the second case a power law dependence. These behaviors are explained with the help of a conductivity model based on the dependence of the tunnel effect on the area of contact.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Electrically conducting composites composed of conducting fillers and insulating polymer matrices have been attracting a great deal of scientific and industrial interest over the last few years [1, 2]. Their many advantages such as control of conductivity, flexibility, lightness, and absorption of shocks, possibly make them suitable for several forms of industrial applications such as electrical conductive adhesive, which replaces the weldings with lead in micro-electronics [3], devices of commutation, shielding, and sensors of pressures. The main advantage of these composites is the abrupt change in the electrical conductivity caused by the variation of either filler content or temperature [4, 5]. At a constant temperature, the composites undergo an insulator to conductor transition when the concentration of fillers increases beyond the percolation threshold. On the other hand, starting from a conductive state, a conductor to insulator transition is observed when temperature increases due to differential dilatation between the polymer and the particles. Many authors [6, 7] have studied the variation of resistivity with applied pressure (piezoresistivity), whether hydrostatic or uniaxial. When pressure is applied, the interparticle separation inside the composite changes, which results in a resistivity change. A new class of material, called magnetorheological elastomers, is made by aligning magnetic particles with the help of a magnetic field before polymerization [8]. These materials

present a 1D percolation and are particularly adapted for mastering the distance between adjacent particles [9]. In this paper, we studied two cases: one where particles are in quasi-contact and the other where they are separated by a polymer layer. These two situations have been obtained by the combined action of magnetic field and temperature during the polymerization process.

2. Experimental methods

2.1. Preparations

The two commercial elastomers we have used are silicone RTV 141A and silicone RTV1062A associated respectively to RTV141B and RTV1062B hardener from Rhone-Poulenc. The fillers are the metallic powders of nickel (5–10 μm size, from MERCK KgaA) and nickel coated silver (10 μm mean size, from Novamet corporation).

The powder is carefully mixed with elastomer, initially by hand and then in a mixer for 1 h to break the maximum of the aggregates and to homogenize the mixture. This mixture was degassed under vacuum for 15 min to eliminate air bubbles and then poured into a cylindrical mold with two brass disks on each side which will be used as electrodes during measurements of resistance. The mixture was rotated during a reticulation process in order to prevent sedimentation of the particles. In the case of mixtures with RTV 141, the time

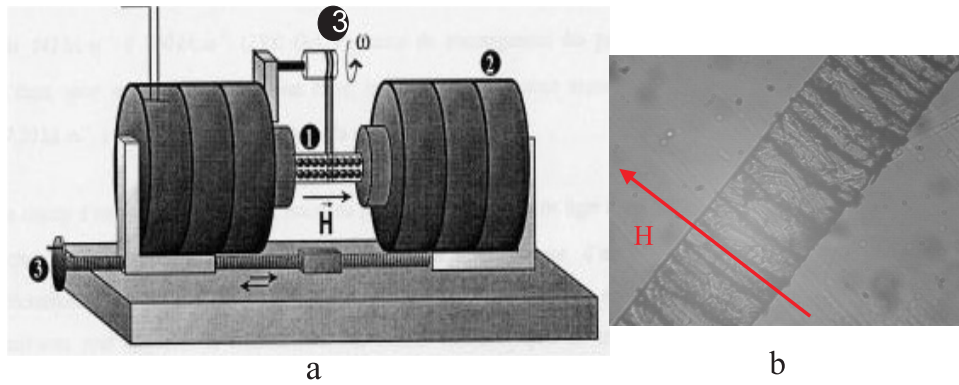


Figure 1. (a) Device for making structured composites. 1: sample, 2: electromagnet, 3: rotation of sample. (b) Example of structured sample (2% Ni-RTV141).

of polymerization can take over 24 h at ambient temperature but less than 1 h when heating at 80 °C. On the other hand, the condition of polymerization for RTV 1062 is only at ambient temperature. Figure 1(a) shows the device used to make the conducting chain structures in the elastomer. The samples are placed between the poles of an electromagnet and the magnetic field is raised progressively until approximately 3000 Oe. Under the effect of this field, the particles align, as we can see in figure 1(b), showing a slice of a structured sample containing 2% in volume fraction. Electrical resistance is measured by means of a HP 3490A digital multimeter. In the case of lower value of resistance, a four-point method using a Keithley 2182A Nanovoltmeter and 6220 current source has been used. All the measurements are performed inside the ohmic region.

2.2. Effect of temperature on the resistivity

In order to show the effect of temperature on the resistivity during cross-linkage, we have compared the resistivity of two composites with the same volume fraction of particles and same elastomer (figure 2). One is cured at ambient temperature and its resistivity is high and approximately equal to that of the second sample cured under heating at 80 °C. Once polymerization was finished, the heating was stopped and variation of resistivity was recorded versus temperature. We notice the strong decrease of resistivity with cooling. The fall of resistivity during cooling can be explained by the difference between the thermal dilatation coefficients of the polymer and the nickel particles. We have measured for the RTV141 without fillers a dilatation coefficient of $3 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$. The total strain of the elastomer matrix when the sample is cooled from 80 to 25 °C should be 0.016. The Young's modulus of the sample has been measured to $E = 700 \text{ kPa}$, so the order of magnitude of internal stresses generated during cooling is 10 kPa. This stress, combined to the hot temperature of curing, allows us to bring particles into contact and then to have a conducting sample at ambient temperature.

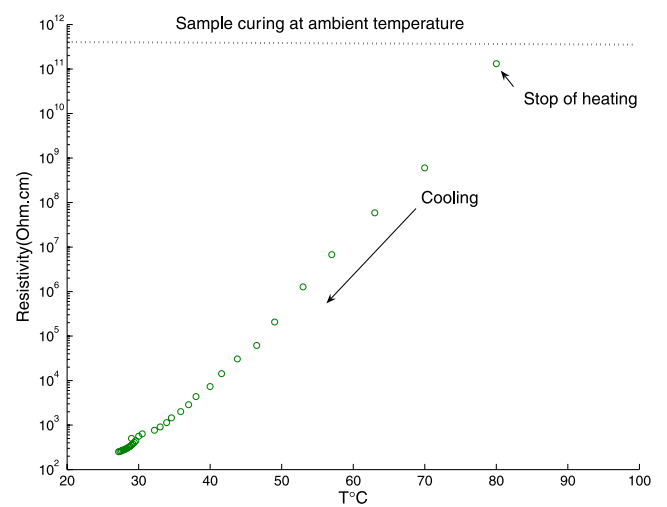


Figure 2. Resistivity of two composites 30% Ni in RTV141. Solid line: composite cured at room temperature, dots: composite cured at 80 °C.

3. Piezoresistivity

3.1. Model of contact resistance

The resistivity of the composites depend on the nature of the contact between adjacent particles. The total resistance is the sum of the constriction resistance and tunnel resistance [10].

$$R = \frac{\rho_{\text{metal}}}{2a} + \frac{\rho_{\text{tunnel}}}{\pi a^2} \quad (1)$$

where ρ_{metal} is the intrinsic particle resistivity, a is the radius of the contact spot and ρ_{tunnel} is the tunnel resistivity which depends on the thickness of the insulating layer between particles and on a work function. According to the analysis of Simmons [11], and Holm [12], the tunneling density of current at low applied voltage is given by:

$$J = \frac{3e^2\gamma}{8h\pi} V \frac{\exp(-\gamma s(x))}{s(x)} \quad (2)$$

with

$$\gamma = 10.24\sqrt{\varphi} \text{ (nm}^{-1}\text{)}$$

where e are the electron charge, h is the Plank constant, V the applied voltage and φ is the height of the potential barrier in eV (0.7 eV for nickel).

For two parallel planes we obtain the tunnel resistivity:

$$\rho_{\text{tunnel}}(s, \varphi) = \frac{8\pi h s \exp(s\gamma)}{3e^2 \gamma}. \quad (3)$$

Now we are looking for the variation of resistance (equation (1)) versus the applied pressure.

3.1.1. Particles initially in contact. If the particles are initially in contact, figure 3(a), the resistance will decrease under pressure due to an increase of contact surface. Due to the large hardness of film oxide, we suppose that the thickness s_0 of this oxide remains constant with pressure and, according to equation (3), the tunnel resistivity will not change with applied load. Depending on whether we are in the elastic or plastic domain we can relate the surface of contact to the applied force.

(i) For elastic deformation

$$R_{\text{elastic}} = 0.57\rho_{\text{metal}} \left(\frac{E}{2rF} \right)^{\frac{1}{3}} + 0.26\rho_{\text{tunnel}} \left(\frac{E}{2rF} \right)^{\frac{2}{3}}. \quad (4)$$

(ii) For plastic deformation:

$$R_{\text{plastic}} = 0.88\rho_{\text{metal}} \left(\frac{H}{F} \right)^{\frac{1}{2}} + \rho_{\text{tunnel}} \frac{H}{F} \quad (5)$$

where, E and H are the Young's modulus and the hardness of the particles respectively, r the radius of particles and F the force between particles.

The plastic deformation occurs when the normal pressure exceeds P_y [13]

$$P_y = \frac{\pi^2(1-\nu^2)^2}{6E} A_y^3 \sigma_y^3 \quad (6)$$

A_y is a function depending only on the Poisson ratio ν and σ_y is the yield stress of the material. For nickel particles, $\nu = 0.3$ $A_y = 1.61$ and $\sigma_y = 900$ MPa giving $P_y = 0.12$ MPa.

3.1.2. Particles separated by a thin film of polymer. When the particles are not in contact and separated by a polymer film figure 3(b), the resistance is only the tunnel resistance. In this case the tunnel resistivity is not constant because the interparticle distance changes with pressure. As we have spherical and not planar surfaces, we must integrate the density of current J on the surface and we obtain [14]:

$$R_p = \frac{8}{3} \frac{h}{e^2} \frac{s_0}{r} \exp(\gamma s_0). \quad (7)$$

If we assume that there are M particles in a chain, separated with the same thickness s_0 , and N conducting chains between electrodes, the total initial resistance of the composite is:

$$R_0(s_0) = \frac{M}{N} R_p = \frac{M}{N} \frac{8}{3} \frac{h}{e^2} \frac{s_0}{r} \exp(\gamma s_0). \quad (8)$$

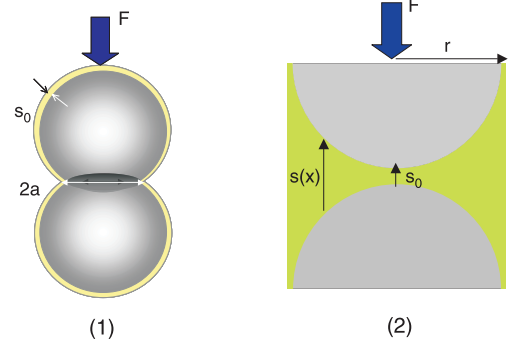


Figure 3. Sketch of two adjacent particles. Figure 1 direct contact between particles with a the contact spot radius and s_0 the thickness of the oxide film. Figure 2 the particles are separated by an insulator film thickness s_0 .

Under pressure, the interparticle separation decreases from s_0 to s and the resistance changes from R_0 to R :

$$\frac{R}{R_0} = \frac{s}{s_0} \exp(-\gamma(s_0 - s)) = (1 - \epsilon_g) \exp(-\gamma s_0 \epsilon_g) \quad (9)$$

where ϵ_g is the local strain between two adjacent particles. This local strain is supposed to be proportional to the macroscopic strain: $\epsilon_g = \alpha \epsilon$, where $\alpha \gg 1$ is a parameter to be determined by fitting experimental data. Finally we get:

$$\frac{R}{R_0} = (1 - \alpha \epsilon) \exp(-\gamma s_0 \alpha \epsilon). \quad (10)$$

3.2. Dependence of piezoresistivity on the matrix

We have seen in section 2.2 that curing at room temperature gives a composite with a high resistivity. If we press it, we expect that the gap between particles will decrease as well as the resistivity. The sample (a cylinder of diameter 20 mm and thickness 2.4 mm molded between two brass disks) is placed below a vertical piston. A force sensor is placed between the piston and the sample and a displacement sensor measures the compression of the sample with a precision of 1 μm . Figure 4(a) compares the piezoresistivity of two composites with the same volume fraction 30% structured at ambient temperature but made with two different polymers RTV141 and RTV1062. It can be seen that the resistivity of composite RTV141 versus applied pressure decreases faster than that corresponding to RTV1062. We can explain this difference of behavior by a different adsorption energy of the polymer on the particle. From the initial value of resistivity and using equation (8), we can estimate s_0 for the two composites. Then we fit experimental data with equation (10) to obtain the parameter α . We find $s_0 = 2.5$ nm, $\alpha = 30$ for RTV1062 and $s_0 = 2$ nm, $\alpha = 80$ for RTV141. If all the macroscopic strain was shared by the interparticle gaps in a perfect linear structure we would expect that $\alpha = 2r/s_0$ which is about 5000. In practice we can have a bending of structures or local rearrangements inside the chains that can expel particles on the side and explain the much lower value of α .

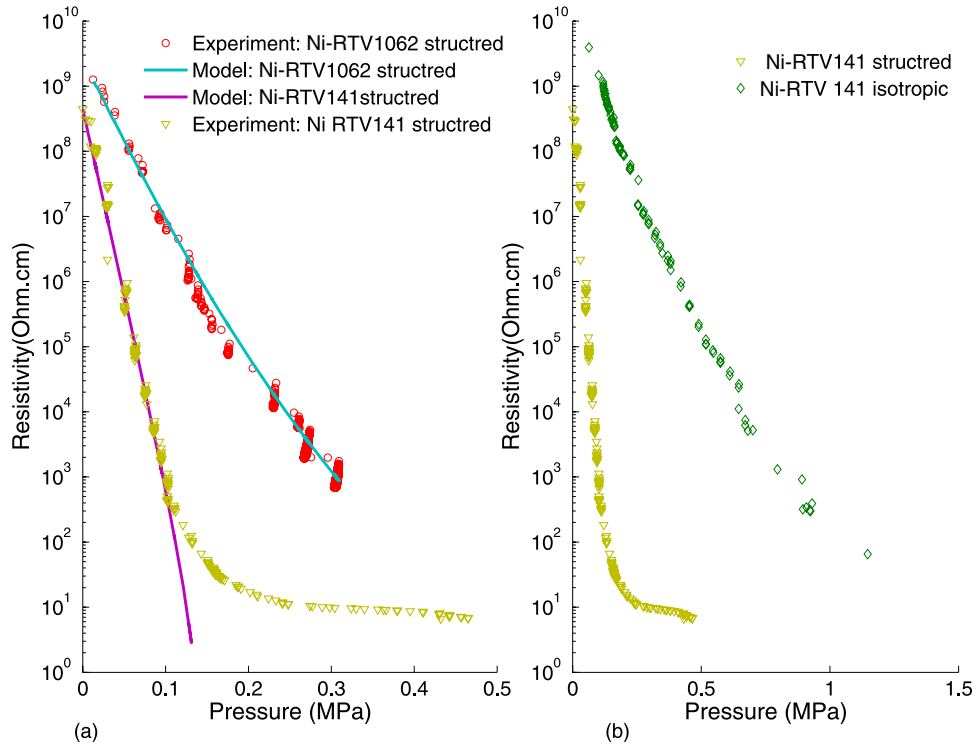


Figure 4. Piezoresistance of composites with the same volume fraction 30%. (a) Samples structured at ambient temperature: the symbols are for the experiment, the straight line indicates the exponential behavior. The parameters of the model are $s_0 = 2.5$ nm and $\alpha = 30$ for RTV1062, $s_0 = 2$ nm and $\alpha = 80$ for RTV141. (b) Comparison of isotropic and structured samples.

3.3. Effect of structure on piezoresistivity

Besides the effect of the matrix on the piezoresistivity we also expect an important difference between a composite where the filler particles are distributed uniformly in the matrix and one where they are aligned.

Figure 4(b) shows the piezoresistivity of isotropic and structured composites containing both 30% in volume of particles in RTV141. We observe firstly that the initial slope of the curve corresponding to the structured sample is much more important than the other one and secondly that their behavior is quite different. For the structured sample there is an exponential decrease followed by a constant value, whereas for the isotropic one, the resistance is continuously decreasing and not in an exponential way. Qualitatively the two domains for the structured sample mean that, in a first step, the interparticle gap strongly decreases and in a second step the particles can rearrange but without compressing further the molecules present at the surface of the particles.

3.4. Role of constriction resistance

In the previous sections we have analyzed the piezoresistivity corresponding to samples cured at ambient temperature with an initial average gap of a few nanometers. Now we are going to consider samples cured at 80°C which present a smaller initial gap. We have used nickel particles coated with silver in order to minimize the oxidation effect. In figure 5 we have plotted the resistivity versus pressure for a structured composite (5% in volume in RTV141). The initial value is much lower than

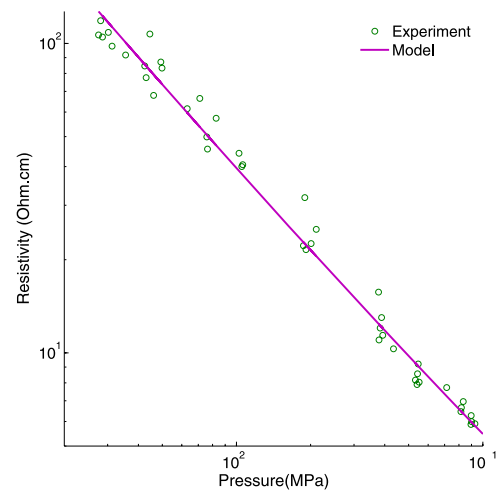


Figure 5. Piezoresistivity of structured composite 5% cured under heating at 80°C . The dots represent the experiment and the solid line the model with $E = 100$ GPa, $\rho_{\text{metal}} = 7 \times 10^{-6}$ Ω cm, $H = 740$ MPa, and $f = 0.7$.

in the preceding case and now the resistivity follows a power law versus pressure (with a power of -0.86) instead of an exponential one. This coefficient is between $(-1/3)$ for the constriction resistance with elastic contact equation (4) and (-1) for the tunnel resistance with plastic contact equation (5), so the model for fitting the experiment is a combination of (4) and (5). We assume that at zero load the resistivity, which is $\rho = 150$ Ω cm, is entirely a tunnel resistivity. Then from

equation (7) we found $s_0 = 0.9$ nm and from equation (3) $\rho_{\text{tunnel}} = 5 \times 10^{-7}$. With this value of ρ_{tunnel} , we find that we can neglect the constriction terms in (4) and (5) for all the range of pressure we have used. We have seen that the yield pressure was 0.12 MPa, which is the upper range of applied pressure, so we could expect a power law of -0.66 instead of -0.86 . Nevertheless, the actual pressure applied on a pair of particles can vary locally and if we introduce a fraction f of elastic contacts and $1 - f$ of plastic contacts the total tunnel resistance will be given by:

$$R = 0.26f \frac{M}{N} \rho_{\text{tunnel}} \left(\frac{NE}{2rF} \right)^{\frac{2}{3}} + (1 - f) M \rho_{\text{tunnel}} \frac{H}{F}. \quad (11)$$

We obtain good agreement with the experiment taking a fraction 0.7 of elastic contacts, which seems reasonable, taking into account that we are mainly in an elastic domain for applied pressure less than 0.1 MPa.

4. Conclusion

We have studied the piezoresistivity of MR elastomers containing Ni particles. Two different regimes have been found. The first one is an exponential decrease with the pressure, corresponding to the compression of a polymer layer between particles for a composite cured at ambient temperature. The second regime shows a power law dependence corresponding mainly to an elastic deformation of

the surface of contact when the polymer is cured under heating at 80 °C. Both behaviors correspond to a tunnel resistance, they are well reproducible and show little hysteresis. The model will be improved in future work to take into account the presence of collapsed chains of particles.

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