

AN EXHAUSTIVE CHARACTERIZATION OF QUANTUM TUNNELLING CONDUCTIVE COMPOSITE

G. Canavese^{1*}, S. Stassi^{1,2}, M. Lombardi¹, A. Guerriero^{1,3}, C.F. Pirri^{1,3}

¹ IIT Istituto Italiano di Tecnologia @ PoliTo, Center for Space Human Robotics, Torino, Italy

² Politecnico di Torino, Department of Physics, Torino, Italy

³ Politecnico di Torino, Department of Materials Science and Chemical Engineering, Torino, Italy

* Corresponding author (giancarlo.canavese@iit.it)

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1. General Introduction

Piezoresistive composite materials have found extensive potential application in the fields of micro-sensors, electromechanical device, circuit breakers and tactile sensors for robotics, providing cheaper, accurate and faster alternatives to devices already present on the market [1-4].

Piezoresistive hybrid materials can be obtained by mixing an insulating polymer matrix with conductive fillers such as metal particles, carbon black, carbon nanotubes, and ceramic particles [5-9]. As concerns the conductive mechanisms, these composites filled with a dispersed conducting phase should be divided in two main families. In the former, well-known as pressure conductive rubbers, the variation of the electrical conduction is due to the change in the contacts among the conducting particles [5, 10, 11]. Previous works have been proposed different percolation models to describe the variation in resistivity as a function of filler concentration [2, 12]. Applying an external load to the composite sample the conductive particles start to aggregate producing connections of particles coming into intimate contact. This provides conductive paths across the sample and the conductivity rises. These models generally fail below the percolation threshold where they predict that the composite is an insulator [13].

On the other hand, in hybrid piezoresistive polymers (known as quantum tunneling composites) the conductive filler particles are well separated each from the others, being fully coated by the insulating matrix, and no conducting paths form. The mechanism of conduction results in the field assisted Fowler-Nordheim tunneling, because the charge injected in the composite reside on the fillers,

generating very large electric local field at the tips on the surface. This novel hybrid material was reported for the first time by Bloor et al. showing a giant change in resistance when compressed [13, 14].

This work presents a wide investigation of the piezoresistive response of an innovative metal-polymer composite. This is based on nickel conductive filler particles dispersed in a polydimethylsiloxane (PDMS) insulating elastomeric matrix. The presence of nanostructured, extremely sharp tips on the nickel particles surface, as shown in Fig.1, is responsible of the local charge density enhancement. This increase guarantees the extreme large variation of the electrical conduction in response to a mechanical strain. Without any mechanical deformation the composite presents an insulating electric behavior, even above the expected percolation threshold, because the polymer intimately coats the nickel particles, avoiding any physical contact among them. When subjected to compression, the particles come closer, without touching each others, and the resistivity decreases of various orders of magnitude.

2. Experimental and method

Nickel powder and polydimethylsiloxane (PDMS) were respectively supplied by Vale Inco Ltd. (Type 123) and Dow Corning Corporation (SYLGARD 184).

In order to prepare pure silicone samples, the PDMS copolymer and the curing agent were mixed with a ratio of 10:1 by weight. The mixture was then degassed at room temperature and cured in a mold at 75 °C for two hours.

The composite samples were prepared dispersing 300-500 parts per hundred resin (phr) by weight of

metal particles in PDMS copolymer. A vigorous mix could disrupt the nanometric tips on the particles surface, drastically reducing the piezoresistive response of the composites. In order to avoid this, the blend was gently mixed [13]. Then, the curing agent was added to the mixture in the ratio 1:10 by weight respect to the PDMS copolymer. In order to avoid bubbles formation, the resulting paste was degassed for 1 hour under vacuum at room temperature. After that, the composite paste was poured in PMMA molds and it was thermally cured in oven at 75 °C for ten hours. Field Emission Scanning Electron Microscopy (FESEM) images on pure Ni powder and composite samples were collected by a field emission scanning electron microscopy (Zeiss SupraTM).

TGA analyses were performed with a METTLER TGA/SDTA 851 instrument between 25 and 800 °C with a heating rate of 10 °C /min in air.

The viscoelastic properties of materials were studied by using a dynamic mechanical thermal analyzer (DMTA, Rheometric Scientific MKIII instrument), at a frequency of 1 Hz in the tensile configuration. This analysis supplies information about:

- the Young's storage modulus (E'), which measures the energy stored elastically,
- the internal damping or loss tangent ($\tan \delta$), which measures the ratio of energy lost to energy stored in a cyclic deformation ($\tan \delta = E''/E'$) [15].

The maximums in $\tan \delta$ are used for the determination of glass transition temperature (T_g) [15, 16].

The gel content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84.

Electromechanical characterizations on the samples with different thickness and PDMS nickel powder ratio were performed using a universal mechanical testing machine (MTS Qtest 10), coupled with a Keithley 2635A sourcemeter connected to a home-made sample holder.

3. Results

The Ni particles used as fillers in these conductive composites are characterized by an irregular surface, as shown in Fig.1. The particles, in fact, present a

spherical-like shape with very sharp nanometric spikes on the surface (even hundreds of nanometer long) that are responsible of the very large electric local field enhancement. The Ni particles have diameters in the range 3.5-7.0 μm , as declaimed by the supplier, and their tendency to aggregate was observed.

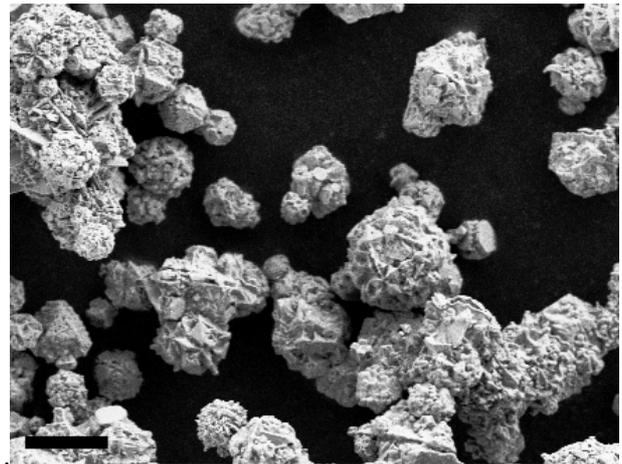


Fig.1. Field Emission Scanning Electron Microscopy (FESEM) image of pure Ni powder. The scale bar corresponds to 5 μm

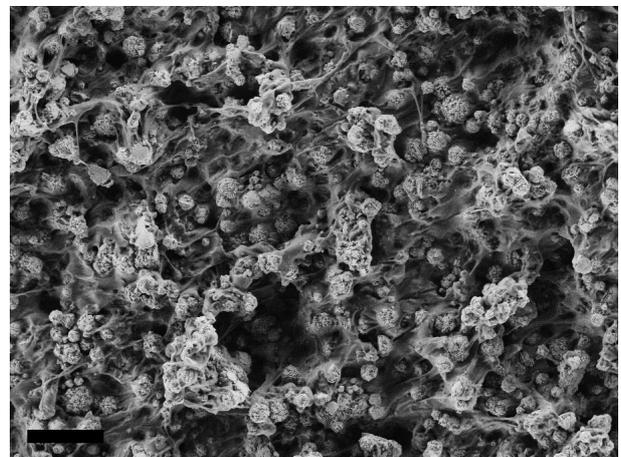


Fig.2. FESEM image of the PDMS-Nickel composite. The scale bar corresponds to 10 μm

The mechanical mixing of the Ni powder with the polymer is able to break the aggregates and assures a uniform dispersion of the particles in the polymeric matrix, as shown in Fig.2. In addition, FESEM image of the PDMS-Ni composite shows that after the mixing the surface morphology of the particles does not significantly changed. More vigorous mixing could ruin the original sharp nanometric

protrusions and determine a reduction of the piezoresistive response [13].

From the TGA data, the onset temperature of the thermal decomposition is detected considering the temperature corresponding to the 10% (T_{90}) weight loss. The pure PDMS (10:1 copolymer-curing agent ratio) begin to degrade at about 460 °C, as revealed by TGA measurements (Fig.3). An enhancement of the thermal stability of the composite materials is observed, respect to the pure PDMS sample. In fact, in the case of the composites the 10 % weight loss is recorded at 540 °C. A single-step decomposition takes place in all the samples, with higher residues for composite materials due to the metallic filler.

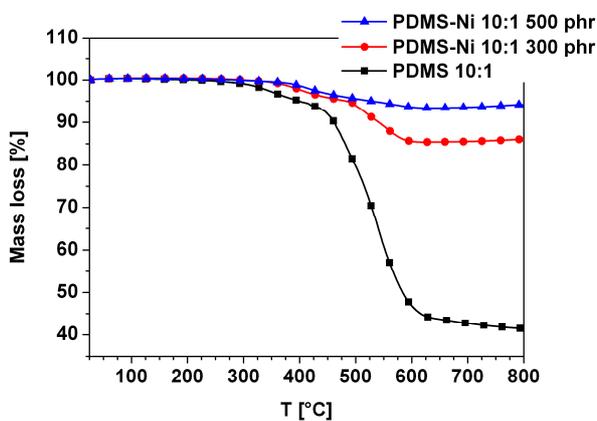
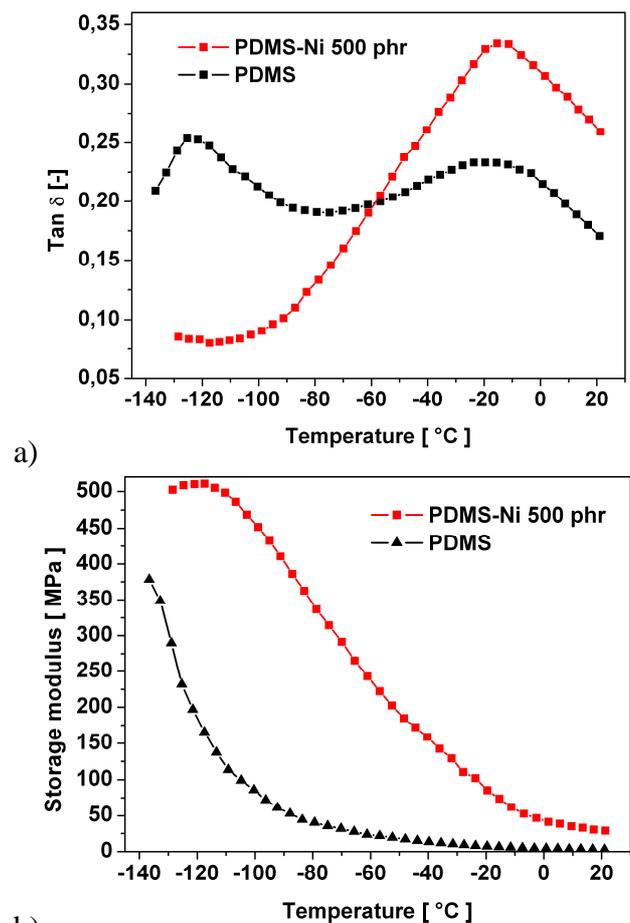


Fig.3. TGA analyses of pure and composite PDMS materials

The elastic (E') and viscous (E'') components of the pure and composite materials (prepared with PDMS 10:1 copolymer-curing agent ratio) in the temperature range -140 – 20 °C are evaluated by dynamic mechanical characterization (Fig.4).

As reported in Fig. 4a, the $\tan \delta$ curve of the pure PDMS sample presents two maximums: the former at about -125 °C corresponds to the T_g of the rubber, the latter at -20 °C represents the melting temperature (T_m) [17]. In Fig. 4b it is possible to observe a strong decrease of E' in the T_g region of the PDMS sample and no increase is observed at higher temperatures. This demonstrates the relatively good curing of the sample. In fact, an incomplete curing of a polymer should show an increase in the modulus due to reactions between unreacted functional groups and curing agent [16]. In the case of the composite material (500 phr), only a

maximum is present in the $\tan \delta$ curve, coinciding with the T_m of the pure PDMS. The Ni particles imply a slight increase in melting temperature which reaches -15 °C in the composite materials. PDMS-Ni materials undergo a reduction of E' at higher temperatures with respect to the pure rubber, probably due to the presence of the metal particles. Also in this case a complete crosslinking of the rubber is achieved.



b) Fig.4. DMTA analyses of pure and composite PDMS (10:1 copolymer-curing agent ratio) materials: a) $\tan \delta$, b) storage modulus.

The gel content test confirms that the presence of Ni particles does not affect the formation of a cross-linked network. In fact high gel content values (above 96 and 93 % for pure PDMS and composites, respectively) are measured. This indicates the absence of extractable oligomers in the cured systems, also in the composites containing a high amount of the metal particles (up to 500 phr).

Electromechanical characterizations in compression load are performed on samples having an area of $10 \times 10 \text{ mm}^2$ and different thickness values or compositions. All the tested composites present a huge variation (from six to nine orders of magnitude) of the electrical resistance when a pressure is applied (from 0 to 1.5 MPa).

The piezoresistive response is strictly related to the mobility of the nickel particles in the polymer matrix. To increase the probability of tunneling of the electrons, the insulating layer placed between two closed particles has to be deformed and thinned by the external load. This behavior is tested by comparing the variation of the electrical resistance under uniaxial pressure for samples prepared with different PDMS copolymer-curing agent ratio (3.33:1 and 10:1) that correspond to different Young's modulus of the obtained elastomer [18, 19]. As reported in Fig. 5 the piezoresistive response is lower for the samples with a lower content of the copolymer, since a more cross-linked polymer i.e. higher stiffness is obtained [20]. Consequently, the reduction of the gap between the conductive particles is more hindered. The effect is higher in the composite with a lower content of metal particles. In this case a higher polymer content is present and the amount of PDMS among metal particles increases. For example the composition 300 phr reported in Fig.5 presents a large variation of resistance in the sample with the low content of curing agent and no piezoresistive response in the sample with the higher one. Moreover, during the mixing process, the 3.33:1 PDMS has a lower viscosity in the liquid form, therefore it can fill better the empty gaps among the particles (particles covering is challenging and difficult due to the presence of spiky protrusion on the surface) increasing the insulating layer [21].

Other parameters able to influence the variation of the electrical resistance are the quantity of the metal filler and the thickness of the sample [22], as shown in Fig.6. As expected, the samples are more sensible to the pressure if the content of nickel is higher, because the particles are closer each to others.

In order to employ this composite as sensing material in a sensor device, the characterization of samples having different thickness was performed since the knowledge of the functional behavior related to the physical dimension is fundamental.

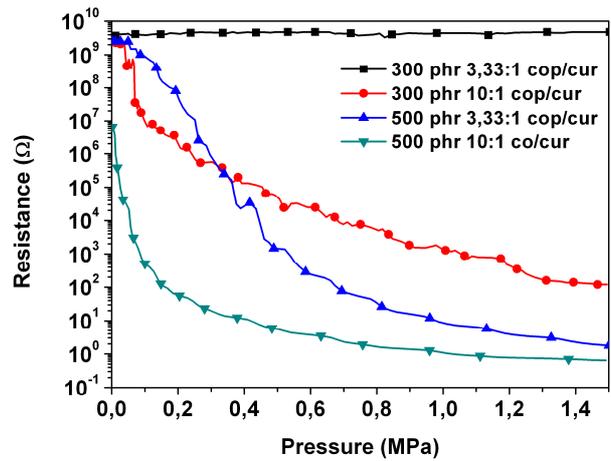


Fig.5. Electrical resistance versus uniaxial pressure of 2 mm thick Ni-PDMS samples as a function of PDMS composition and nickel content

For these composite materials, the relationship between resistance and thickness is highly nonlinear (Fig.6), contrarily to the second Ohm's law. The resistance dependence on the thickness is varying with the applied uniaxial pressure, because the deformation of the composite is strongly dependent on its initial shape and dimensions. For this reason the data presented in this work are referred to values of resistance instead of resistivity.

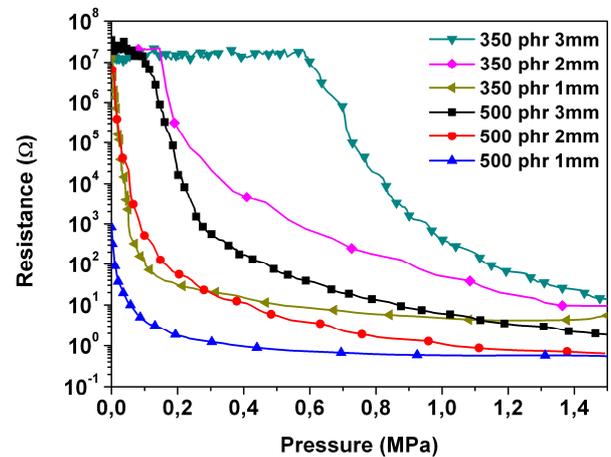


Fig.6. Electrical resistance versus uniaxial pressure of Ni-PDMS samples, prepared with PDMS copolymer-curing agent 10:1, as a function of thickness and nickel content

Dynamic electromechanical characterizations are performed to test the material reusability and measurement repeatability. Samples are tested through 10 cycles of compression and decompression at different frequencies of the

applied load. The elastic behavior of the material allows the composite to completely recover the initial form and particles disposition after every cycle, restoring the resistance value for the insulating state. On the contrary, the resistance value in the maximum compression state shows a small increase during the whole measure, probably due to hysteresis and creep phenomena during the load cycles (Fig.7). Another evidence of these typical polymeric phenomena is the increase of the electrical resistance at maximum pressure by increasing the velocity of uniaxial compression [23].

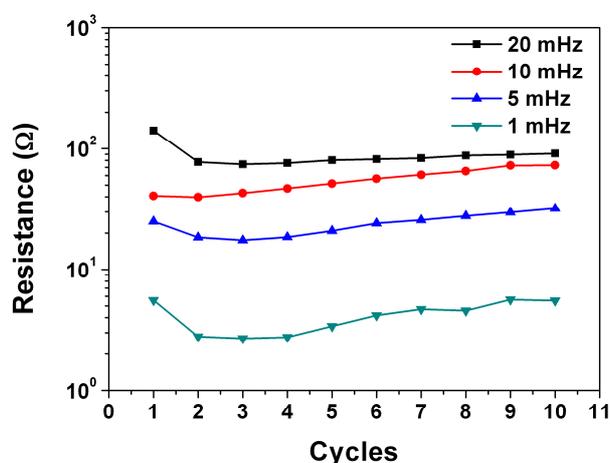


Fig.7. Minimum electrical resistance values of composite samples (500 phr of Ni powder, 2 mm thickness and 10:1 copolymer/curing agent ratio) obtained for 10 cycles of compression and decompression at different frequencies.

4. Conclusions

A comprehensive investigation of an innovative piezoresistive composite based on PDMS filled with spiky Ni particles has been presented.

FESEM images prove that the composite fabrication process preserves the sharp nanostructures on the surface of the Ni particles and that they are intimately coated by the polymeric matrix. Even for very high filler loading the samples present an insulating electrical behavior in undeformed state.

Viscoelastic properties have been investigated by DTMA. Gel content as well as thermogravimetric analyses of the composites have been conducted.

The electrical resistance of the composite, evaluated in function of different process parameters, is found to be extremely sensitive to mechanical compressive load. Moreover the repeatability of the piezoresistive

response as a function of a variable uniaxial load was reported.

Cost efficient materials, simplicity of the process, large sensibility and harsh environment compatibility make these composites good candidates as sensitive elements in several applications that require wide deformation, low power consumption and easy conformability.

References

1. Wilson, S.A., et al., *New materials for micro-scale sensors and actuators: An engineering review*. Materials Science and Engineering: R: Reports, 2007. **56**(1-6): p. 1-129.
2. R. Strumpler and J. Glatz-Reichenbach, *Conducting Polymer Composites*. Journal of Electroceramics, 1999. **3**(4): p. 329-346.
3. Dahiya, R.S., et al., *Tactile Sensing - From Humans to Humanoids*. Robotics, IEEE Transactions on, 2010. **26**(1): p. 1-20.
4. B. C. Muñoz, S. Gregory, and S. Steven, *Conductive polymer-carbon black composites-based sensor arrays for use in an electronic nose*. Sensor Review, 1999. **19**: p. 300-305.
5. X. Niu, et al., *Characterizing and patterning of pdms-based conducting composites*. Advanced Materials, 2007. **19**: p. 2682-2686.
6. W. Luheng, D. Tianhuai, and W. Peng, *Effects of conductive phase content on critical pressure of carbon black filled silicone rubber composite*. Sensors and Actuators A: Physical, 2007. **135**(2): p. 587-592.
7. W. Luheng, D. Tianhuai, and W. Peng, *Influence of carbon black concentration on piezoresistivity for carbon-black-filled silicone rubber composite*. Carbon, 2009. **47**(14): p. 3151-3157.
8. Spitalsky, Z., et al., *Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties*. Progress in Polymer Science, 2010. **35**(3): p. 357-401.
9. Jeong, D.-Y., et al., *Piezoresistive TiB₂/silicone rubber composites for circuit breakers*. Sensors and Actuators A: Physical, 2009. **149**(2): p. 246-250.
10. Souza, J.F.G., R.C. Michel, and B.G. Soares, *A methodology for studying the dependence of electrical resistivity with pressure in conducting composites*. Polymer Testing, 2005. **24**(8): p. 998-1004.
11. Q. W. Yuan, et al., *Simulations on the reinforcement of poly(dimethylsiloxane)*

- elastomers by randomly distributed filler particles*. Journal of Polymer Science Part B: Polymer Physics, 1996. **34**(9): p. 1647-1657.
12. F. Carmona, *Conducting filled polymers*. Physica A: Statistical Mechanics and its Applications, 1989. **157**(1): p. 461-469.
 13. D. Bloor, et al., *A metal-polymer composite with unusual properties*. J. Phys. D: Appl. Phys., 2005. **38**: p. 2851-2860.
 14. Lantada, A.D., et al., *Quantum tunnelling composites: Characterisation and modelling to promote their applications as sensors*. Sensors and Actuators A: Physical, 2010. **164**(1-2): p. 46-57.
 15. Ehsani, M., et al., *An investigation of dynamic mechanical, thermal, and electrical properties of housing materials for outdoor polymeric insulators*. European Polymer Journal, 2004. **40**(11): p. 2495-2503.
 16. Mafi, R., et al., *Cure characterization of epoxy and polyester clear powder coatings using Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA)*. Progress in Organic Coatings, 2005. **54**(3): p. 164-169.
 17. Voulomenou, A. and P.A. Tarantili, *Preparation, characterization, and property testing of condensation-type silicone/montmorillonite nanocomposites*. Journal of Applied Polymer Science, 2010. **118**(5): p. 2521-2529.
 18. D. Armani, C. Liu, and N. Aluru. *Re-configurable fluid circuits by PDMS elastomer micromachining*. in *Micro Electro Mechanical Systems, 1999. MEMS '99. Twelfth IEEE International Conference on*. 1999.
 19. Quaglio, M. and et al., *Evaluation of different PDMS interconnection solutions for silicon, Pyrex and COC microfluidic chips*. Journal of Micromechanics and Microengineering, 2008. **18**(5): p. 055012.
 20. Fu, S.-Y., et al., *Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites*. Composites Part B: Engineering, 2008. **39**(6): p. 933-961.
 21. Ausanio, G., et al., *Giant resistivity change induced by strain in a composite of conducting particles in an elastomer matrix*. Sensors and Actuators A: Physical, 2006. **127**(1): p. 56-62.
 22. G. Canavese, et al., *Comprehensive characterization of large piezoresistive variation of Ni-PDMS composites*. 2010 IEEE ISBN: 978-1-4244-8770-7
 23. S. Stassi, et al., *Giant Piezoresistive Variation of Metal Particles Dispersed in PDMS Matrix*. MRS Proceedings, (2011). **1299**(s09-05).