AN INNOVATIVE COPPER-PDMS PIEZORESISTIVE COMPOSITE FOR FLEXIBLE TACTILE SENSOR

S. Stefano[1,2*], G. Canavese[1], F. Cosiansi[2], M. Cocuzza[1,2,3]

[1]*Center for Space Human Robotics@PoliTo, Istituto Italiano di Tecnologia, C.so Trento 21, 10129 Torino, Italy*
[2]*Department of Applied Science and Technology, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy*
[3]*CNR-IMEM, Parco Area delle Scienze 37, 43124 Parma, 43124, Italy*
**stefano.stassi@polito.it*

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Abstract
A composite material based on multi branch spiky copper particles dispersed into silicone matrix was prepared as functional material for piezoresistive tactile sensor. The material showed giant variation of electrical resistance under the application of both compressive and tensile forces with a sensitivity tunable with variation on the process parameter as filler amount and sample thickness. A flexible matrix tactile sensor was realized with a simple and fast combination of soft lithography and hot-embossing techniques using copper metalized polyimide films as electrodes.

1 Introduction
Piezoresistive materials have been a research focus for the last decade as sensitive materials for a wide range of applications, i.e. electromechanical sensors, micro actuators, tactile sensors for robotics, touchable sensitive screen etc. providing cheaper, accurate and faster alternatives for devices already present on the market [1-3]

During the last years, research efforts have been oriented toward hybrid composites, where carbon black, graphite flakes, fibers and various metal powders, such as Zn, Ni, Cu, Ag and Fe, have been used as active fillers [4-7].

Two kinds of piezoresistive composites should be distinguished as a function of the conduction mechanism among the dispersed phase. The former composite type, also known as pressure conductive rubber, exhibits a variation of the electrical conduction in response to a mechanical deformation, as a consequence of the contact change among the conductive particles [8]. To describe the formation of conductive paths under external load, originated by intimately contacted particles, different percolation models have been proposed [9, 10]. Generally, these models fail below the percolation threshold where they predict that the composite is an insulator [11]. The latter piezoresistive composite type (known as quantum tunneling composite, QTC) show a conduction mechanism that can be well represented by field assisted Fowler-Nordheim tunneling model. Here the filler particles are well separated among each others, being fully coated by the insulating polymeric matrix [4, 12].

This work presents a wide investigation of the piezoresistive response of an innovative metal-polymer composite based on copper conductive filler particles dispersed in a polydimethylsiloxane (PDMS) insulating elastomeric matrix. The copper particles are

intimately coated by the polymer that avoids any physical contact between them. The presence of nanostructured, extremely sharp tips and multi branch structure on the copper particle surface, promote an electrical field enhancement and consequently a reduction of the potential barrier width of the Fowler-Nordheim tunneling conduction. This results in an insulating electric behavior when no mechanical deformation is applied to the composite, even above the expected percolation threshold [11]. When subjected to compression, the thickness of the insulating layer between the particles is reduced and the resistivity decreases of various orders of magnitude.
To the best of our knowledge for the first time a giant piezoresistive response in nanostructured copper-silicone composite was measured and the prepared material was applied as sensitive layer in tactile device.

2 Materials and testing methods

Copper powder and bi-component polydimethylsiloxane (PDMS) were supplied by Pometon Ltd. (Type LT10) and Dow Corning Corporation (SYLGARD 184) respectively.
Field Emission Scanning Electron Microscopy (FESEM) observations of the copper powder showed particles in the range of 10-20 μm, presenting a highly irregular surface. The particles present multi branch microstructures covered by very sharp spikes (up to few micrometers long) as shown in Fig.1a.
The composite samples were prepared by dispersing from 150 to 250 parts per hundred resin (phr) by weight of metal particles in PDMS copolymer. A vigorous mix could disrupt the tips on the particles surface, drastically reducing the piezoresistive response of the composites [11]. In order to avoid this, the blend was gently mixed at room temperature. Then the PDMS curing agent was added to the mixture in the ratio 1:10 by weight respect to the PDMS copolymer. The resulting paste was outgassed for 1 hour under vacuum at room temperature to remove any trace of bubbles, poured in Poly(methyl methacrylate) PMMA molds realized by milling techniques and then cured in oven at 70°C for three hours.
Electromechanical characterizations on the samples under compressive and tensile forces were performed using a universal mechanical testing machine (MTS Qtest 10), coupled with a Keithley 2635A sourcemeter connected to a home-made sample holder.
The samples for the compression analysis were realized with a square footprint of 10x10 mm^2 and different thicknesses. They were placed between two stiff copper plates fixed to the grips of the test machine, working as electrodes. For the tensile functional characterizations, pieces of electrical conductive copper tape were clamped between each sample, in its undeformed state, and the universal test grips. The sample strips used for the tensile tests were 5 mm wide, 40 mm long and 1 mm thick.

3. Results and discussion

The mechanical mixing of the copper powder with the polymer assures a uniform dispersion of the particles in the polymeric matrix, as shown in Fig.1b. FESEM observations on the copper-PDMS composite showed that the surface morphology of the particles does not significantly change after the mixing. Furthermore no tendency of aggregation was observed and all the particles were completely covered by the polymer.
The conductive mechanism inside the composite is attributed to quantum tunnelling phenomena and is enhanced by the morphology of the particles, presenting very sharp spikes on the surface [4, 12]. The particular shape of the copper powder helps the polymer to intimately coat the filler, avoiding physical contact between close particles. Therefore the composite presents an insulating electric behavior in his undeformed state. While when the composite is compressed, the insulating layer between the particles is reduced causing an

increase of the probability of the electron tunnelling. Consequently the resistivity of the sample decreases exponentially.

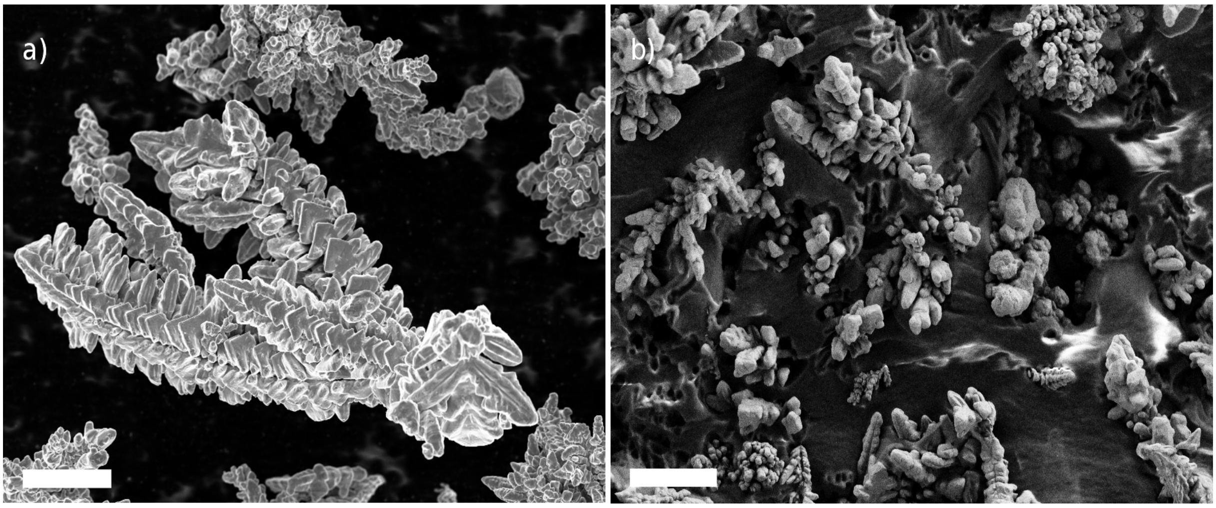

Figure 1. Field Emission Scanning Electron Microscopy (FESEM) images obtained a) on the copper powder and b) on the copper-PDMS composite. The scale bars correspond to 10 µm.

The piezoresistive response is strictly related to the mobility of the copper particles in the elastomer 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. Since the PDMS used in this work is a bi-component, the Young's modulus of the obtained composite can be tuned varying the copolymer-curing agent ratio [13]. Then the sensitivity of the final material to the applied pressure would be lower for composition with a lower content of copolymer, since a more cross-linked polymer with higher stiffness would be obtained [14]. The effect is higher in the composite with a lower content of metal particles, because the amount of PDMS among metal particles amount increases. Previous works on other metal-silicone composites [12] have shown that the 10:1 copolymer-curing agent ratio, that has been selected for the copper-PDMS, can guarantees an optimum stiffness for the sensitivities requested in tactile applications.
Furthermore the functional properties are strongly dependent on the thickness of the final samples and on the quantity of metal filler, as reported in the graphs in Fig.2. In order to employ this composite as sensing material in a sensor device, the influence of the thickness was evaluated since the knowledge of the piezoresistive behavior related to the physical dimension is fundamental. The composite material presented a highly nonlinear relationship between resistance and thickness (Fig.2a). The deformation of the samples is in fact strongly dependent on the initial condition of shape, dimension and composition, while the composite resistance in the undeformed state is the same for any thickness. The sensitivities of the 200 phr composite with different thickness, computed from the slope of an exponential fit of the curves varies from 53 mΩ/kPa and 270 mΩ/kPa of 2 mm and 1mm respectively, up to 200 Ω/kPa for the 0.5mm sample.
For what concerns the dependence of the piezoresponse on the metal content, the pressure sensitivity of the composite increases with higher filler quantity. The particles become closer to each others in the undeformed state (i.e. decrease the thickness of the potential barrier), then the same resistance values can be obtained with lower pressures respect to composite with less filler quantities. As shown in Fig.2b, without any applied pressure all the composition have a resistance higher than 100 MΩ, confirming that the copper particles are completely covered by an insulating layer of polymer and there are no conductive paths inside the composite. While under compression the composites suffer different variations of

resistance, depending on the copper content, that could be as high as nine orders of magnitude in the 250 phr composition. The evaluated sensitivities of the different compositions were 8 mΩ/kPa for the 150phr, 270 mΩ/kPa for the 200 phr and 5 Ω/kPa for the 250 phr.

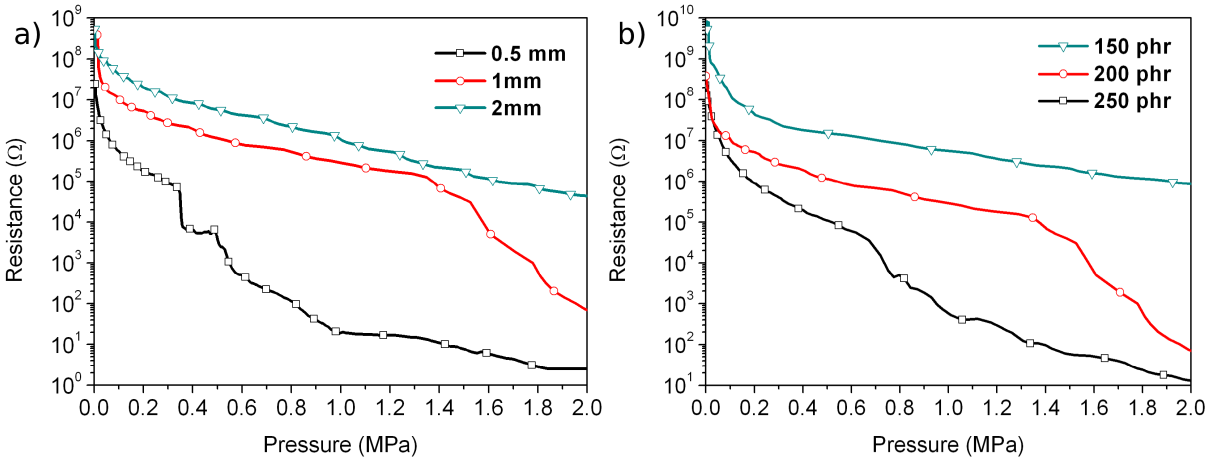

Figure 2. Electrical resistance versus uniaxial pressure of copper-PDMS samples, prepared with 10:1 PDMS copolymer-curing agent ratio, as a function of a) thickness (copper content of 200phr) and b) copper content (thickness of 1 mm).

Variation of electrical resistance of the material was registered also under the application of a tensile force. When elongated in one direction, the strip of composite contracts in the directions perpendicular to the applied pressure by keeping the volume constant. This would result in a thickening of the interparticle layers in the direction of the applied force and a reduction of the gaps between the particles in the other two directions. Since the copper particles are randomly distributed along the material and are not perfectly aligned on planes, a deformation in the direction perpendicular to the force would mean a redistribution of the particles in the composite that can create tunnelling paths along the samples. Then the resistance of the strip would decreases exponentially with the applied tensile deformation by following the tunnelling conduction mechanism. Evidences of this phenomenon are reported in Fig.3 where a strip of composite prepared with 250 phr composition was cyclical elongated and then relaxed at different percentages starting monotonically from 10% up to 40%. After the first deformation, the following measurement presented an enhancement of the electrical resistance circa in correspondence of the end of the previous applied deformation. This behavior is attributed to the presence of the Mullin effect, a typical phenomenon observed in filled rubbers [15]. Evidence of the Mulling effect was measured also in stress-strain characterization since the mechanical response of the composite strip was dependent on the maximum loading previously encountered.

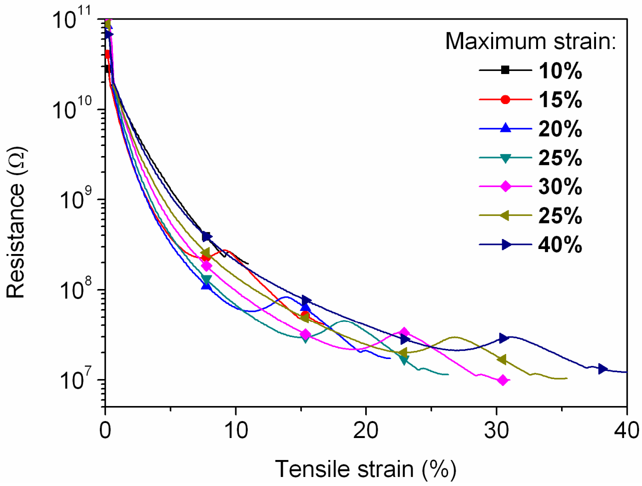

Figure 3. Electrical resistance versus elongation of copper-PDMS strips, prepared with 10:1 PDMS copolymer-curing agent ratio, as a function of the maximum elongation.

In order to obtain the functional material in the form of self-standing multilayered thin samples and to promote the sensor spatial resolution and the piezoresistive sensitivity, a process flows based on soft lithography and hot-embossing techniques was optimized [16]. A sketch representing the process flow used for the fabrication of tactile sensor is reported in Fig. 4. The electrodes were realized from copper metalized polyimide films with a standard lithography technique. The films were coated by positive photoresist and then parallel lines 3mm thick and 3mm far from each others were patterned by UV lithography. The metal was then selectively etched in an Iron (III) chloride bath and the photoresist removed with acetone. The flexible tactile sensor was then realized by pouring the composite mixture in hollow PMMA molds embedded between two polyimide films placed orthogonally to form an electrode matrix. Subsequently the multilayer was pressed and heated for 3 h at 70 °C until the composite material was reticulated.
The prepared flexible tactile sensor was then tested in all the nodes (crossing of the electrodes), obtaining a piezoresponse comparable with the previous reported characterizations. Cross-talking measurements were also performed by applying a compressive force on one element of the matrix and measuring the resistance in the first closing ones. No remarkable variations from the undeformed value resistance were registered.

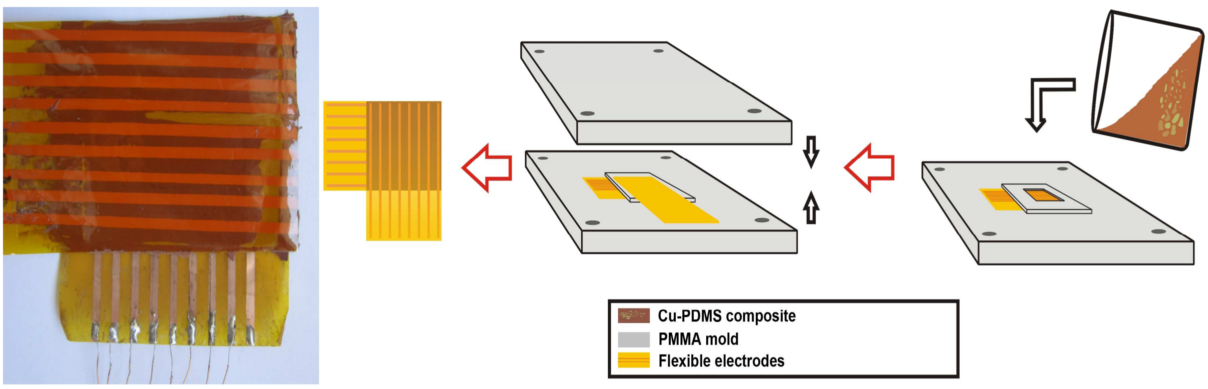

Figure 4. Image of the copper-PDMS sensor and hot embossing process flow: pouring of the mixture in the PMMA mold, pressing and heating.

4.Conclusions

A comprehensive investigation of an innovative piezoresistive composite based on PDMS filled with spiky copper particles has been presented. FESEM images prove that the composite fabrication process preserves the sharp protuberances on the surface of the metal filler. The polymer intimately coating the copper particles guarantees, even for very high filler loading, an insulating electrical behavior of the composite in undeformed state. The electrical resistance of the composite is found to be extremely sensitive to mechanical stimuli, both compressive and tensile load. The piezoresponse has been studied changing several process parameters in order to tune the composite sensitivity for different applications. Modifying the thickness and the composition of the composite samples, the sensitivity has been varied from few mΩ/kPa up to hundreds of Ω/kPa. After the functional characterizations, the material has been used for the realization of flexible matrix tactile sensor with a simple, fast and economic hot embossing process. Cost efficient materials, simplicity of the process, large sensibility, and harsh environment compatibility make this composite a great alternative to the traditional materials used in tactile sensing based on capacitive, magnetic and piezoelectric principles.

References

[1] Yousef H., Boukallel M., Althoefer K. Tactile sensing for dexterous in-hand manipulation in robotics - A review. *Sensors and Actuators, A: Physical*, **167**, pp. 171-187 (2011),

[2] Jiang M. J., Dang Z. M., Xu H. P. Significant temperature and pressure sensitivities of electrical properties in chemically modified multiwall carbon nanotube/methylvinyl silicone rubber nanocomposites. *Applied Physics Letters*, **89**, pp. 182902 (2006),

[3] Nambiar S., Yeow J. T. W. Conductive polymer-based sensors for biomedical applications. *Biosensors and Bioelectronics*, **26**, pp. 1825-1832 (2011),

[4] Abyaneh M. K., S.K. Kulkarni S. K. Giant piezoresistive response in zinc–polydimethylsiloxane composites under uniaxial pressure. *J. Phys. D: Appl. Phys.*, **41**, pp. 135405 (2008),

[5] Zhou J. F., Song Y. H., Zheng Q., Wu Q., Zhang M. Q. Percolation transition and hydrostatic piezoresistance for carbon black filled poly(methylvinylsilioxane) vulcanizates. *Carbon*, **46**, pp. 679-691 (2008),

[6] Paul D. R., Mark J. E. Fillers for polysiloxane ("silicone") elastomers. *Progress in Polymer Science*, **35**, pp. 893-901 (2010),

[7] Pierre C., Deltour R., Van Bentum J., Perenboom J. A. A. J., Rammal R. Electrical-conduction mechanisms in polymer copper-particle composites. II. (1/f)-noise measurements in the percolation limit. *Physical Review B*, **42**, pp. 3386-3394 (1990),

[8] Ausanio G., Barone A. C., Campana C., Iannotti V., Luponio C., Pepe G. P., Lanotte L. Giant resistivity change induced by strain in a composite of conducting particles in an elastomer matrix. *Sensors and Actuators A: Physical*, **127**, pp. 56-62 (2006),

[9] Hussain M., Choa Y.-H., Niihara K. Conductive rubber materials for pressure sensors. *Journal of Materials Science Letters*, **20**, pp. 525-527 (2001),

[10] Ding T., Wang L., Wang P. Changes in electrical resistance of carbon-black-filled silicone rubber composite during compression. *Journal of Polymer Science Part B: Polymer Physics*, **45**, pp. 2700-2706 (2007),

[11] Bloor D., Donnelly K., J Hands P., Laughlin P., Lussey D. A metal–polymer composite with unusual properties. *J. Phys. D: Appl. Phys.*, **38**, pp. 2851-2860 (2005),

[12] Canavese G., Lombardi M., Stassi S., Pirri C. F. Comprehensive characterization of large piezoresistive variation of Ni-PDMS composites. *Applied Mechanics and Materials*, **110-116**, pp. 1336-1344 (2012),

[13] Quaglio M., Canavese G., Giuri E., Marasso S. L., Perrone D., Cocuzza M., Pirri C. F. Evaluation of different PDMS interconnection solutions for silicon, Pyrex and COC microfluidic chips. *Journal of Micromechanics and Microengineering*, **18**, pp. 055012 (2008),

[14] Fu S.-Y., Feng X.-Q., Lauke B., Mai Y.-W. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites. *Composites Part B: Engineering*, **39**, pp. 933-961 (2008),

[15] Diani J., Fayolle B., Gilormini P. A review on the Mullins effect. *European Polymer Journal*, **45**, pp. 601-612 (2009),

[16] Canavese G., Stassi S., Stralla M., Bignardi C., Pirri C. F. Stretchable and conformable metal–polymer piezoresistive hybrid system. *Sensors and Actuators A: Physical*, in press.