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Filled Polysilsesquioxanes:
A New Approach to Chemical Sensing

*Anna Castaldo,** *Ettore Massera, Luigi Quercia, Girolamo Di Francia*

Summary: In an attempt to investigate new polymeric materials as constituents of an e-nose we focus our attention on a new emerging class of versatile three-dimensional polyhedral silicon polymers, called polysilsesquioxanes, containing nanosized inorganic cages. Such hybrid amphiphilic materials offer exceptional opportunities to create composites with singular properties. In particular we found that the polyhedral organosilsesquioxane (POSS) cages covalently attached to the polymer backbone as side-chain act as an ''internal'' filler with a nanometric homogeneous dispersion. We show how it is possible to fabricate sensing devices based on selected POSS matrix and, by a suitable choice of other "external" home-made fillers, (e.g. graphite, copper, silicon, zinc and their alloys) obtained by mechanical milling the response of the resulting composites towards different classes of compounds can be tuned. In particular we fabricated a new high sensitive relative humidity device, exhibiting a fivefold response change for relative humidity changing in the range 0% to 100%. This behaviour can not be modelled on the basis of the matrix swelling operating mechanism. Rather, the combined effect of the matrix and the filler has to be invoked in order to explain the formation of nanopores inside the material that are responsible of the porous behavior of our sensors.

Keywords: fillers; POSS; relative humidity (RH); sensors; silsesquioxane

Introduction

In the past many papers have appeared in literature describing the use of electronic nose based on array of sensors, singularly low selective, used to characterize analyte mixtures.[1] Often in such devices polymer-carbon black composites have played a very important role by virtue of their simply manufacture and cheapness.[2] The mechanism of response in polymer carbon-black composite sensing films is, at its simplest level, based on film swelling. Vapours absorbed in the film cause its swelling, disrupting conductive pathways by pushing carbon particles apart, thus increasing the electric resistance of the film. The polymers used in the first-generation of electronic nose were selected based only on statistical analysis, chemical functionality being very rarely considered.[3] Clearly, polymer selection greatly depends on the suite of target compounds. If target compounds represent a broad distribution of chemical functionalities, then a broad distribution of polymers will be necessary. Unfortunately, the use of a single filler, i.e. carbon black, could hamper the possibility to adopt a given class of polymers as a result of the possible incompatibility between polymer solvents and dispersant agent for that kind of filler. If fillers dispersion is not good enough sensor devices are affected by electronic noise. At the same time, the very nature of the polymer is another cause of such noise.[4] For this reason in the sensor field there is a continue effort to study new polymer composite that could be stable, sensitive, selective and exhibiting the lowest possible noise. In this frame we have

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decided to direct our basic research towards the polysilsesquioxanes, a class of nano-composite polymers that are receiving increasing interest in the nanoscience/nanotechnology field.[5,6,7]. As a matter of fact the incorporation of silsesquioxane cages or POSS, polyhedral organic silsesquioxanes, into a polymer matrix results in significant improvements in a variety of physical and mechanical properties, due to reinforcement at the molecular level of the inorganic ceramic like framework. In the polymeric sensors field, silsesquioxane can not enter as fillers, like carbon black, because they are not conductive. But we assumed that introducing POSS cages in a polymer by means of covalent bonds and using external conductive fillers could yield new nanostructured composites to fabricate our sensor devices. The versatility of the POSS molecule and the more than one hundred demonstrated compatible polymer systems makes however a no simple task the choice of a proper polymer matrix to fabricate sensors. Anyway, starting from our previous experience in composite sensors and taking advantage of simple chemical considerations we chose the Poly [(propylmethacryl-hepta-isobutyl-POSS)-*co*-(*n*-butylmethacrylate)]. Heptaisobutyl and butyl chains grant for a weak dipolar (WD) character, while siloxane and methacrylic group furnish hydrogen-bond basic (HBB) properties. This, in general, makes such a polymer a versatile matrix for polymer composite sensors. Moreover the use of a same matrix to sense different analytes could offer the possibility to treat electronic noise, in an hypothetical e-nose based on an array of such polymer composites as a systematic error.

For this study we excluded carbon black because sensors obtained with this kind of filler were too much noisy. Rather we worked to synthesize carbonaceous nano-fillers, like graphitic powder and its alloy with metals like zinc and copper and silicon.

It is worthwhile to note that BM permits to obtain nanocrystalline metal alloys with properties that are undoubtedly quite different from the equilibrium intermetallics.[8] Our idea to fabricate different proprietary nanometric fillers has been to mix carbonaceous conductive products and metals by ball milling processes, obtaining alloys acting as active filler in a polysilsesquioxane composite. Alloy of graphite-silicon, graphite-copper, graphite-zinc in various ratios have been investigated. A further advantage of home-made fillers is that optimisation of the filler dispersion in the polymer matrix is in general an iterative process, that requires several different steps such as testing the performance, or reducing its dimensions, surface area and porosity, until satisfactory results are obtained.

Experimental Part

Some of the fillers used in this work were obtained by planetary ball milling technique[9] performed in ambient atmosphere in stainless steel or agate jars filled with balls of the same material and placed in a charge ratio of 1:10. Roto-revolution speed ranging from 200 to 450 rpm and time of reaction from 2 hours to 6 hours were investigated. The average dimension of the obtained graphite and silicon powder were 500 nm. Once fabricated copper micrometric (300 micron) powder by ball milling, to further reduce its dimension we added in the same jar an equal amount of micrometric graphite and we performed ball milling to obtain a homogeneous nanometric alloy. Zinc was a commercial nanopowder purchased by Sigma-Aldrich. Raman Spectra were obtained using a Raman Renishaw model 2000 instrument. Spectra were collected in back scattering configuration at T ambient (source operating at 514,4 nm power 10 mW). FIB experiments were performed with a FEI Quanta 200 3D equipment. Samples were deposited by spinning on silicon substrates. Poly [(propylmethacryl-heptaisobutyl-POSS)-*co*-(*n*-butylmethacrylate)] 15% POSS cages purchased by Sigma Aldrich was dissolved in THF. Fillers were

suspended in THF, then polymer solution and filler suspension were mixed by means of sonication. 2 mL of the suspension were spun on a glass substrate rotating at 4000 rpm. Resulting polymeric films were 500 nm thick. Over these film 3000 Å thick gold contacts were deposited by e-gun evaporation. Sensors devices were characterized by a test chamber already described.[10]

Results and Discussion

Composite films used in this work are based on Poly [(propylmethacryl-heptaisobutyl-POSS)-*co*-(n-butylmethacrylate)] with 15% POSS cages reported in Figure 1 and conductive fillers, home made by ball milling techniques, tailored for the best dispersion in the polymer itself.

Figure 2 shows SEM images of some of the fillers used in this study. They are graphite, zinc, copper-graphite, respectively.

All fillers used are characterized by micro-Raman technique to verify if in the milling experiment an amorphization or chemical reaction between the particles had occurred: ball milling in fact is a mechanochemical process, somewhere used to promote reaction in conditions far from

equilibrium (non thermodynamics).[11] In Figure 3 Raman analysis of graphite, silicon and their 1:1 alloy is reported. We observe that graphite and silicon are crystalline powders and in the alloy spectrum there are all the expected peaks, so that no reaction between carbon and silicon is supposed to have occurred.

We fabricate several sensor devices as described in the experimental part, using a 20% wt of external fillers and test their performance with respect to relative humidity, hexane and ammonia. As a matter of fact we can describe our system as based on an intrinsically nanostructured polymer with ''internal'' filler covalently attached and ''external'' homogeneously dispersed conductive fillers. Interestingly, POSS could self-assemble into crystals or aggregates in the polymer matrix in which they are incorporated as substituent side units, and POSS crystals or aggregates have an important effect on its properties.[12] The extent of POSS crystallization can be controlled by the processing condition, which indicated that the morphology in the polymer matrix is mainly dependent on the competition of the POSS intermolecular interaction and the polymer backbone constraint to limit POSS crystallization. To evaluate the degree of dispersion of POSS fillers in the films used as sensors we perform a FIB analysis. The Ga^+ ion bombardment selectively removes POSS cages leaving holes. Film retain its morphology and in Figure 4 we can note that these holes are homogeneously placed in our film. This gives an indirect evidence of the morphology of the material.

In Figure 5 the response to water vapour in the 30%–70% range of relative humidity of the device based on a 20% graphite nanocomposite film is reported. As it is possible to observe, the device response is quite high and the sensor rapidly and reversibly follows RH variations, increasing its conductivity in presence of water molecules.

This unusual behaviour suggests that sensor device does not work on the swelling mechanism (decrease of conductivity in
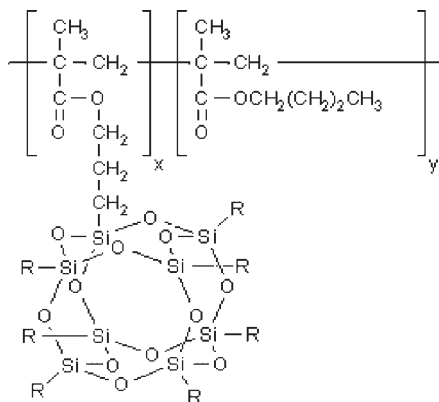
R = i-Bu, x = ~0.1, y = ~0.9

Figure 1.
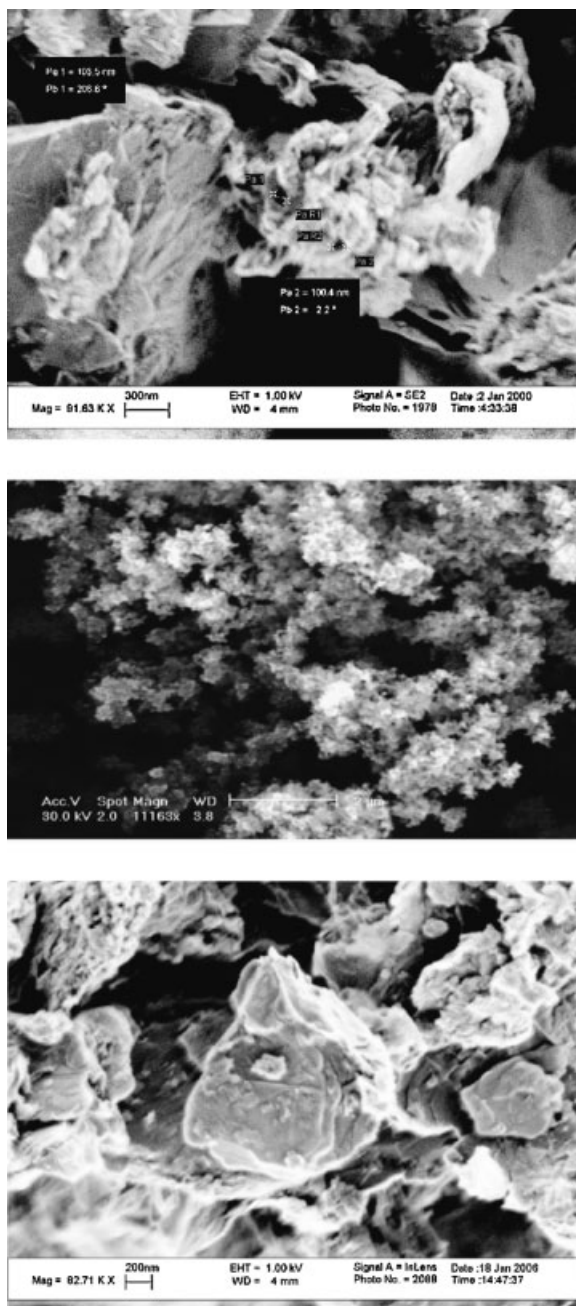Poly [(propylmethacryl-heptaisobutyl-POSS)-co-(n-butylmethacrylate)].

Figure 2.
SEM photographs of graphite, zinc, copper-graphite fillers used in this work.

presence of the analyte). It is important to note that we also tested the POSS without external fillers and even in this case we observed an increase of its conductivity in presence of water molecules. This furthermore points towards a more complicated mechanism involving POSS cages. In our opinion secondary fillers promote a local
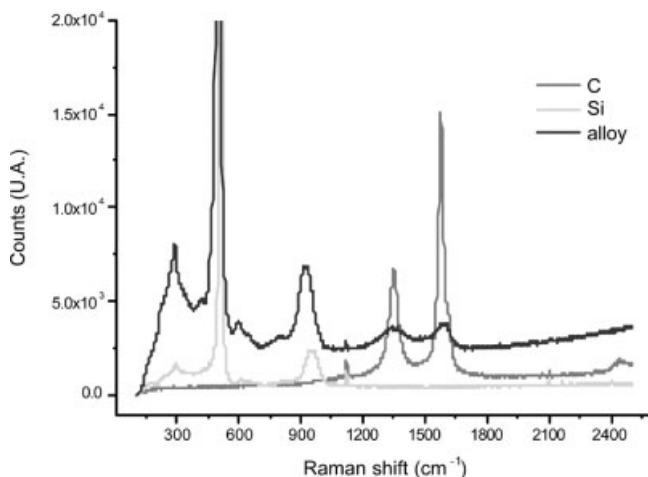
Figure 3.
Raman analysis of graphite, silicon and silicon-graphite (1:1) alloy.

structuration of these cages that creates voids or pores, where analytes molecules could be hosted, as it is suggested by the fact that with transitions metallic filler, device performance with respect to relative humidity is very good (see Figure 6), giving evidence of a probable coordination effect of the metals.

Another interesting aspect of POSS based device is the wide conductivity variation range. In Figure 6 it is reported the response in the full RH range for devices obtained with different fillers (Zn-Graphite, Zn, Cu, Silicon-graphite) where the five fold magnitude variation between 0% and 100% RH in the conductivity of the sensors is shown. In the same figure the response of the device in which no external filler is used (cyan line) is reported. Even in this case we observe an increase of the device conductivity with respect to water molecules but the response is worse and a large hysteresis is shown. Noticeably the best performance is
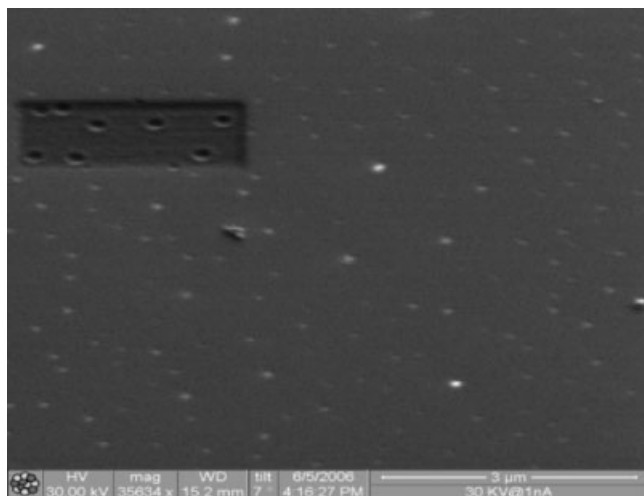

Figure 4.
FIB photograph of a POSS based composite after ions beam striking.
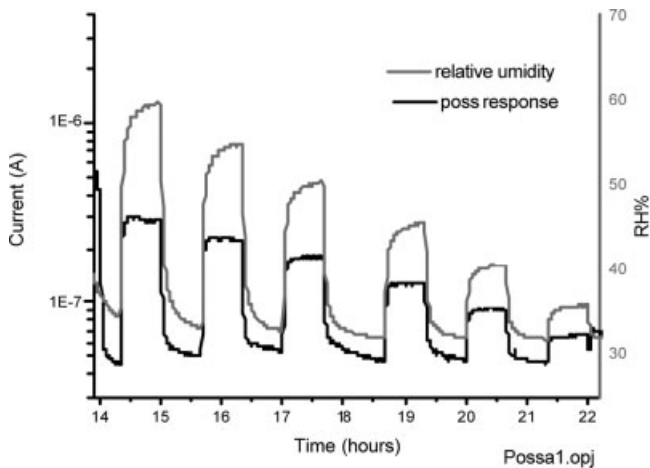
Figure 5.
Device response to RH of the graphite filled POSS.

obtained with Zinc and Copper based fillers.

Sensors devices have been also tested in presence of apolar vapours, like hexane, to verify the versatility of the matrix.

In Figure 7 response to hexane in anhydrous ambient of different devices is reported. It is possible to observe, even in this case an increase of the conductivity in presence of the analyte. Operating mechanism of these sensors is still under investigation. Preliminary results seem to indicate the formation of a pore network, due to

relative disposition of POSS cages, that can be influenced by external fillers.

Conclusions

In this work we present polymeric nano-composite sensors, based on a POSS matrix properly selected and nanostructured compatible fillers, that exhibit excellent sensing properties and could be used in the sensing of both polar and apolar analytes. In particular we obtain new RH sensors with
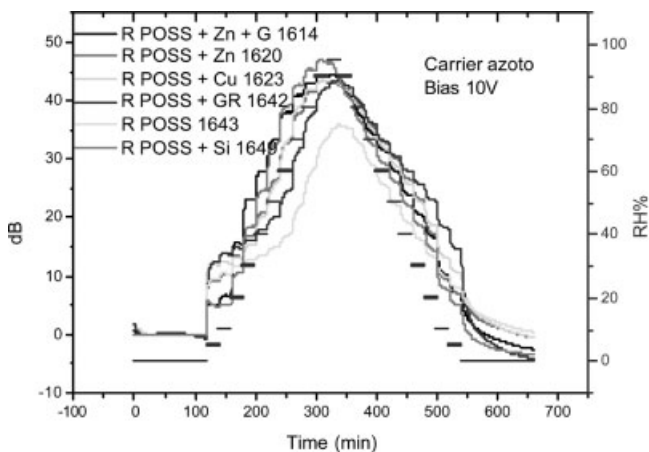

Figure 6.
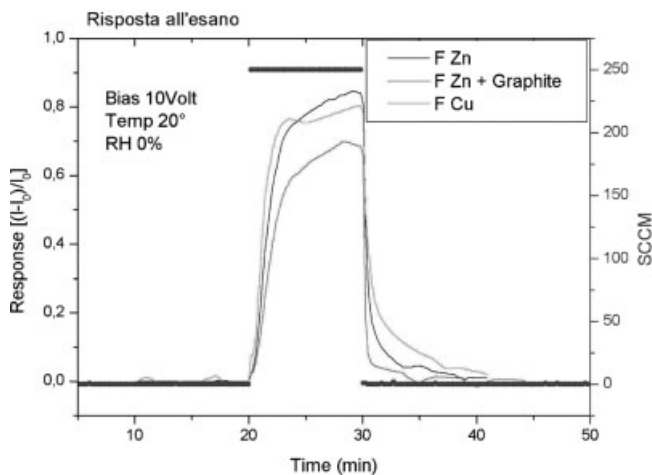Performance in the humidity sensing of devices in logarithmic scale.

Figure 7.
Response to hexane of various devices.

different filler (Zn, Zn-Graphite, Si, Cu-Graphite), whose conductivity varies of various magnitude orders between 0% and 100%. Sensor responses can not be modelled on the basis of the matrix swelling operating mechanism. Rather the combined effect of the matrix internal and external filler has to be invoked in order to explain a porous-like behaviour.

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