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DESIGN OF A BULK CONDUCTIVE POLYMER USING EMBEDDED MACROSCOPIC COPPER CELLS

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ABSTRACT

This paper introduces a technique of inducing bulk conductivity in a polymer. The technique uses coiled copper 'cells' embedded into a polymer during fabrication which can subsequently create highly redundant series-parallel networks. The preceding body of work aimed to improve the conductivity of non-conducting polymers by embedding particulates (of metal, carbon, etc.) into the polymer, or by altering the polymerization chemistry to incorporate conductive elements. The technique described here keeps the process independent of the specific polymer chosen by not relying on the polymerization chemistry to aid in the incorporation of the cells. The embedding drastically lowers the resistivity of the polymer, from 10^{12} Ω-cm (approx.) for pure silicone rubber to less than 50 Ω-cm for the composite at room temperature: a drop of 12 orders of magnitude. A secondary consideration of this paper is the mechanical stiffness changes brought about by the embedding of metal inside a flexible polymer. Although the connected network of copper cells allows the rubber to be highly conductive in bulk, the cells are themselves compliant and thus have minimal effect on the stiffness of the cured silicone rubber.

INTRODUCTION

Conductive polymer composites attempt to merge the useful conductive properties of metals with mechanical properties of polymers. Polymers traditionally have high corrosion resistance, elasticity, and tensile strength. Polymer composites attempt to incorporate the high conductivity of metals into a polymer base matrix while retaining these useful properties. Also, polymers are relatively cheap and accessible; hence they are used in a wide variety of applications. Conductive polymer composites find uses in static discharge membranes covering device surfaces, electrical shielding barriers, and absorbers of electromagnetic radiation. Such polymers with especially high conductivity and sensitivity to loading forces can act as transducers, converting mechanical deflections to electrical signals through a change in conductivity. This paper develops the design of a polymer-independent internal skeleton (Fig. 1) to be embedded into a polymer (Fig. 2) in order to improve lower its resistivity.

A. Chemical Doping

Although most polymers are excellent dielectrics and find use as insulators, intrinsically conductive polymers do exist. A well-known example is Polyaniline, which has been the subject of considerable research since the 1980's when MacDiarmid demonstrated that chemical redox reactions to doped parts of the polymer chain (with Emeraldine base) decreases the resistivity of the polymer significantly (from the 10^{10} Ω-cm to 1 Ω-cm with 20% dopant)[1].

Fig. 1 A random packing of 300 cells

Fig. 2 A polymer sample with 300 embedded cells

While these polymers can achieve relatively high conductivity with appropriate doping, the native forms of these polymers do not conduct very well: Polythiophenes and Polyacetylenes have resistivity in the range of 10^8 Ω-cm to 10^{10} Ω-cm [2].

Shirakawa et al. showed that semiconducting polymer trans-polyacetylene $(CH)_x$ shows marked increases in conductivity after undergoing halogenation by bromine or iodine vapor. The trans- isomer was used in these experiments because it is thermodynamically stable at room temperature and has a lower resistivity than the cis- isomer Exposing films of trans-polyacetylene to iodine vapor caused a change in resistivity from 2.3 x 10^4 Ω-cm to 10^{-3} Ω-cm [3]. This work demonstrated that polymer-halides have the potential to be highly conductive relative to the native polymer.

A slightly different procedure is to perform the doping during polymerization as demonstrated by Penner using pyrrole (or thiophene) electro-polymerized within an ionically conductive Nafion-impregnated Gore-Tex membrane [4]. The composite polymer has the mechanical properties of the Gore-tex membrane and the electrical properties of polypyrrole. Polypyrrole, made of heterocyclic monomers, is intrinsically conductive. Nafion-impregnated Gore-tex, whose native resistivity is extremely high, electropolymerized with pyrrole, whose native resistivity is between 10^{-2} Ω-cm and 10^{-1} Ω-cm, produces a composite that has resistivity between 2 x 10^{-2} Ω-cm and 5 x 10^{-2} Ω-cm [4].

B. Carbon-black infused films

Carbon black has been widely used as a polymer filler because it provides stability to polymer matrices as a colorant and as an antioxidant promoting the longevity of rubber [5]. In recent years it has been used to introduce conductivity in polymers as well [6]. Studies by Lacasse et al. [7] demonstrated that as increasing mass fractions of carbon black are added, silicone 940-carbon composites reach resistivities as low as 10^2 Ω-cm. Similar studies by Huang [5] showed that with polypropylene and ethylene-octene copolymer, the resistivity fell to about 10^5 Ω-cm starting from the same initial 10^{16} Ω-cm resistivity for the polymers alone.

Therefore it is seen that blending carbon-black particles of the right sizes lowers the resistivity considerably for these polymers. The samples tested in experiments using thin-films demonstrate a percolation mechanism using carbon black that results in low resistivity above a certain threshold in the percentage of dopant [8].

C. Metal-polymer compaction

Gurland et al. reported [9] that compacting a mixture of powders comprising of polymeric insulator (Bakelite-polyoxybenzylmethylenglycolanhydride) and a metallic conductor (silver) gave a product that had an electrical conductivity much higher than the polymer itself when the metal loading was greater than 35% by volume. In these experiments the silver was found distributed randomly in uniform spheres throughout the polymer. This phenomenon was explained using percolation theory. The loading of metal powders (a volume fraction of the entire polymer base matrix) is compared to a random graph where the conducting metal powders are clusters in the graph, and the conduction of the entire polymer is similar to the connectivity of the entire graph using the clusters. Given such, percolation theory predicts that there exists a critical volume fraction above which the conductive clusters create a connected path through the network via which an "element" (charge) can then travel down the connected graph from any one point to another.

The critical threshold that Gurland demonstrated for silver-Bakelite combination (35%) was dependent on the materials used and the degree of compaction used. Mukhopadhay et. al tested a sample of copper powder mixed with poly-(methyl methacrylate) (PMMA) in a similar fashion as Gurland (varying loading amounts of metal in the metal-polymer composite). A similar phenomenon was observed as with Bakelite: the copper-PMMA mixture with metal volume fractions greater than 12% (approx.) had significantly lower resistivity than mixtures with lower loading volume of metal powder and the resistivity decreased until loading percentages increased to 40%. The resistivity of the mixture changed from 10^{13} Ω-cm with no metal addition to 10^3 Ω-cm for 12% metal loading all the way to 10^1 Ω-cm for 40% metal loading [10].

The design process described in this paper addresses the problem of low conductivity in polymers using an inexpensive, efficient method that can be rapidly fabricated without interfering with the polymer chemistry. This allows the process to be independent of the type of polymer used, which may be tied to the application in hand.

DESIGN AND EXPERIMENTAL METHODS

The central design idea was to embed a large number of conductive 'cells' made of a highly conductive metal (copper) in a polymer matrix (silicone) which very high intrinsic resistivity. These conductive cells come in direct physical contact with each other during the fabrication of the composite, and through their number and adjacency, create a quasi-connected network of contact resistances. This highly-redundant series-parallel resistor network provides a medium of charge transfer in the matrix provided the inter-element resistances – effectively the resistance at the contacts – are small. As a result, the composite gains a high level of conductivity while the network of cells simultaneously increases the stiffness of the polymer.

The composite that results from this embedding is not a thin-film conductor, and is scalable to arbitrary sizes and shapes through its high bulk conductivity. Also, the mechanism only requires that the metal chosen has high intrinsic conductivity, making the composite independent of the specific metal or polymer chosen. The choice of polymer and metal can be suited to the mechanical properties desired in the composite. An additional advantage to this method is that the fabrication process is relatively inexpensive.

Investigations were made into the form of the cells embedded in the matrix, the stiffness of cell packing, and the

resistivity of the polymer composite as a variable amount of stress is applied to it.

A. Form and size of embedded cells

Several different choices of copper cells were evaluated for use in embedding: short linear coils, short straight filings, and coiled thin coils (Fig. 3). A desired characteristic of the cell designs is compliance in as many dimensions as possible, such that packings of compliant cells maintain bulk compliance of the polymer.

Simple preliminary testing of the elastic modulus of the cell types indicate that the lowest stiffness and lowest resistivity was achieved for cells made from were coiled thin coils of copper. To fabricate these cells bare copper wire (AWG 30) was wound around a 1.5 mm piano wire (not shown) to from a thin linear coil. This coil was rewound around the same piano wire to form a 'coil-of-coils' (Fig. 4), which was clipped at every 6 mm (approx.) to form cells. Although the cells have bending compliance in all directions, the highest compliance exists in shear as each coil of coils slide along each other and some compliance is exhibited along the radial axis of the larger coil.

B. Stiffness evaluation of packing and composite

The cells are randomly packed into a cast measuring 60mm x 60mm (approximately 100 cells on each 'layer'), and these packings are tested for their stiffness before a polymer is molded around them. The test packing is placed on an Instron [11] which applies a range of strains on the packing while measuring the resultant stress. The average of the stress-strain plots for a given number of cells gives the average Young's Modulus for this number of cells and the packing type. The resistance of the sample is measured after cells are randomly packed in the cast and stress is applied on the packing: this provides information on the change of resistance of the packing when a load ensures greater degree of contact between cells.

Once the packings are evaluated, a preparation of shore 10 silicone [12] is poured onto the cells to cure around the cell skeleton. The cured composite is then tested for its Young's Modulus, providing some insight into the increase in stiffness in the silicone brought about by the internal skeleton of copper cells.

C. Conductivity of composite

The cured samples of composite are compressed by flat-plate electrodes placed on the square faces (base and top) of each sample. Using a standard four-wire resistance measurement technique, the obtained resistances were used to obtain the bulk resistivity of the entire composite sample as it was stressed. The resistance of the composite was compared to the bulk resistivity of the packings alone, and to the known resistivity of silicone 10.

RESULTS AND DISCUSSION

The first design question was the selection of a form and type of cell to use as the embedded element. This was determined through simple measures of resistance for samples of different types of cells embedded in polymers. Additionally, the elastic

Fig. 3 Designs evaluated for the embedded cells: linear coils (left), copper filings (middle) and coiled-coils (right)

Fig. 4 Selected design of cells to be embedded

modulus of these samples was measured. From samples of thin-coils, thick-coils and coil-of-coils, the lowest resistance and highest compliance was observed for samples with embedded coil-of-coils. This design decision was the optimal among the selected candidates, although no theoretical claim can be made about their global optimality.

The exact nature of large packings of these cells was evaluated next. From previous theoretical studies on conductive cell packings [13], a minimum number of cells (300) in a true bulk-conductor was obtained. All subsequent tests use 300 cells, packed randomly in a cast of stated dimensions with approximately 100 cells in each layer of the cast; the mold reached a height of 18mm.

Random packings of 300 cells were poured in a cast (without a polymer) and the resistance of these packings was measured to be $4.24 \pm 0.45\ \Omega$. The randomness of packing configurations accounts for the variance in these measurements. For the specified sample size, the bulk resistivity of the packings can be calculated to be $84.3 \pm 8.96\ \Omega$-cm.

These packings were tested on the Instron for both their elastic modulus as well as the change in resistance with increasing stress.

Fig. 7 illustrates that the aggregate stiffness of the cell packings is low compared to the stiffness of the composite shown on Fig. 8. However, as the strain (deformation) of the cells increases, the gradient of the stress-strain plot (Young's modulus) increases significantly, indicating that deforming the cell packing increases its stiffness as the compliant cells collapse into each other.

Fig. 8 shows the change that the embedded cells bring to the stiffness properties of the original silicone polymer, whose elastic properties are also shown on this figure (dashed line). From the two figures, it can be inferred that the embedding of cells in the polymer matrix increases the stiffness of the polymer. The increase in stiffness over the tested degree of strain can be determined by comparing the final stress achieved over the linear

region of the plots. When the stress for a pure silicone sample is compared to the composite at the same strain value of 0.16 mm/mm, the observed increase in stiffness is a factor of 2.26. Therefore the embedding of copper cells in the silicone matrix increased the stiffness of the polymer by a factor of 2.26.

From Fig. 5 and Fig. 6, we can see the electrical properties of the cells and the composite. Fig. 5 shows the change in resistance measured for random cell packing samples as a variable amount of stress is applied. From the plot and the exponential fit of the data, it is evident that the resistance of the bulk cell packing decreases rapidly with increasing stress as greater and greater numbers of contacts are made between cells. Also, as cells are compressed together at higher stresses, the degree of contact between each cell and its neighbors increases, increasing the area of each contact. This further reduces the resistance at contacts. Note that the resistivity observed for

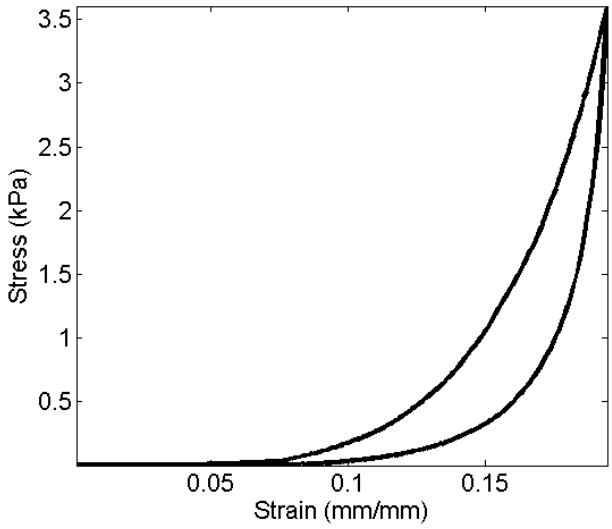

Fig. 7 Stress-Strain curve for a packing of 300 cells

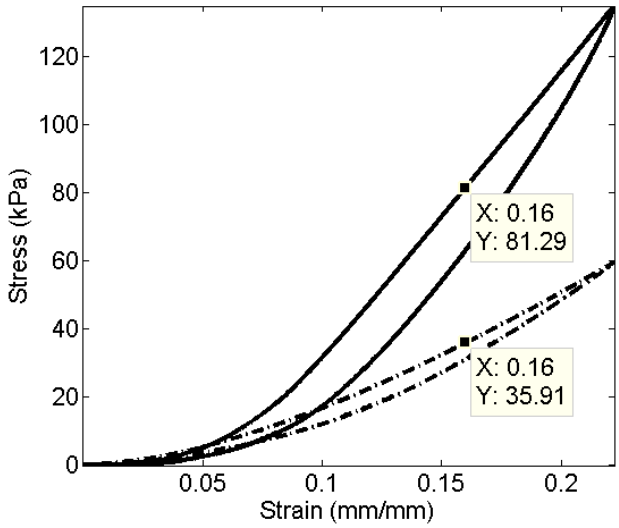

Fig. 8 Stress-Strain curve for composite with 300 embedded cells (solid line) compared with a pure silicone sample of the same dimensions (dashed line)

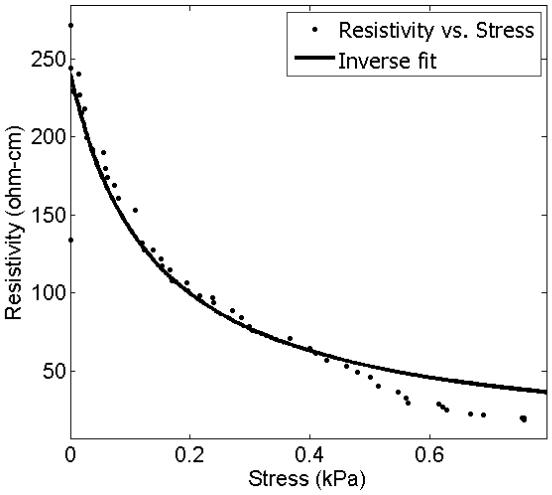

Fig. 5 Resistance-stress plot for 300 cell random packings

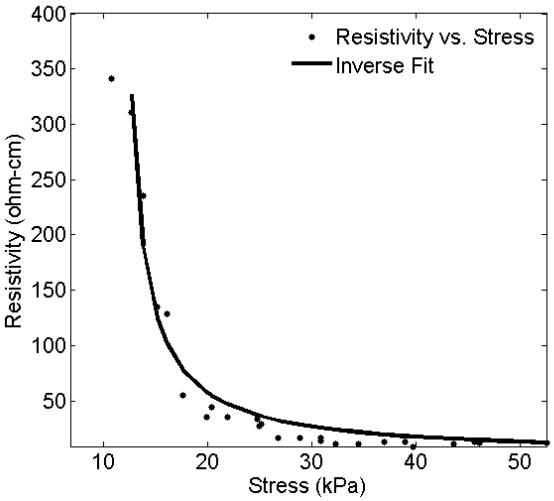

Fig. 6 Resistance-stress plot for a composite sample with 300 embedded cells

random packings of 300 cells in a static scenario with plate electrodes does not represent the y-axis intercept of this plot since the flat plate electrodes applied some stress to the random packings. A more relevant perspective to the resistive properties of the packings is presented in Fig. 6, which accounts for the stresses applied even during the process of measurement. The aggregate behavior of the cells suggests that embedding these cells into a polymer where contacts between cells is possible will create a conductive composite polymer. Additionally, compressing the composite can be expected to result in increasingly better conductivity.

Fig. 6 illustrates the validity of this hypothesis, showing decreased resistance as the composite is compressed. It must be noted that the stress values at which the resistance decreases is much higher for the composite (Fig. 6) than for the packing of cells (Fig. 5). This is to be expected because contacts between cells in the composite are 'worse' than in the packing: as the polymer is poured as a liquid mixture onto the cells, the polymer

is able to seep between the cells and potentially create thin layers at the contacts. Also, the weakened contacts ensure that the inverse relationship of stress and resistance fails to hold at low stresses. The high resistance of the composite at low stress values shows that this is indeed a potential cause of the deterioration in performance. Since the silicone matrix itself has extremely high resistivity, any polymer present between two adjacent cells increase the series resistance at the contact considerably.

CONCLUSION

In the new designed described for conductive polymer composites, highly conductive copper wire was coiled twice to create quasi-spherical cells that were embedded in a silicone matrix. This created a conductive skeleton for the polymer that provides bulk conductivity to the composite. Stiffness tests on the composite and random cell packings illustrated that there was a 126% increase in the stiffness of the composite with the incorporation of the cells compared to the polymer alone. Despite the increase in stiffness, measures of resistance of composite samples as stresses are applied on them showed that bulk-resistivity of less than 50 Ω-cm can be obtained in the composite: an improvement of 12 orders of magnitude.

Future work can attempt to address questions regarding design changes that would provide high conductivity when relatively low stresses are applied, as well as modifications decrease the added stiffness caused by the embedding.

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