Conductive elastomeric composites

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Abstract. Conductive elastic materials are formed by distributing conductive particles within an elastic polymer. We consider a novel composite based on dendritic nickel particles that exhibit remarkably strong negative piezoresistivity with an increase in conductivity of up to 10 orders of magnitude with strains of the order of 0.2. A vital factor for the conductivity of conductive elastomers is the concentration of conductive fillers and many aspects can be understood in terms of percolation theory. In this system the concentration of particles within the composite does not change with strain, yet due to the shape of the particles, the concentration of electrical contacts between the particles does change. We have developed a new model based on the concentration of contact sites, rather than particles which enables us to successfully model this remarkable strain-dependence of conductivity.

1. Introduction
Conductive elastic composites are composites of conductive particles loaded into an elastic matrix in which the conductivity is dominated by the conductive particles [1]. There is a considerable focus in the literature on carbon-based particles, such as carbon blacks, graphite powders and more recently carbon fibres and carbon nano-tubes [2-4]. A variety of phenomena have been observed which include percolation, positive and negative temperature coefficients of resistivity and large strain dependences of conductivity [1,2]. Such electrical measurements have provided insights into the mechanical properties such as the increased stiffness with loading and stress softening [5]. Each of these effects is believed to be determined, to some extent by the formation and breaking of networks of sample spanning chains of inter-connected filler particles [6]. In the case of the effect of strain on carbon black loaded elastomers a number of studies show that there is an initial decrease in conductivity with strain followed by an increase in conductivity with strain > 50% [5-7]. This increase in conductivity is observed for elastic composites with carbon black fillers of high structure, where individual particles are fused aggregates of smaller particles. For composites with lower structure carbon black, the conductivity continually decreases with increasing strain over the whole range of elongation [7]. The strain dependence of conductivity can also be dependent on other factors such as the concentration of conductive particles, the elastic matrix, temperature and method of processing. To our knowledge no detailed mechanism has been presented to explain these variations in conductivity with strain. Percolation theory has been successfully used to explain the change in conductivity of conductive composites with increasing concentration of conductive particles [8,9] with a relationship of the form

\[ \sigma = k(p - p_c)^n \]  

(1)
where $\sigma$ is the conductivity, $p$ the fraction of conductive particles, $p_c$ the critical concentration, $n$ the critical exponent and $k$ a constant. For conductive composites, $p_c$ depends on the structure and distribution of the conductive particles in the matrix [9] and $n$ is often found to be $\sim 2$ [10].

In this paper, results for a conductive elastomer composite with highly structured metal filler particles are presented and we demonstrate the striking negative piezo–resistance displayed by this material. We develop a new approach which applies percolation theory to a system with a fixed concentration of conductive particles but with a strain related concentration of conductive contacts between particles.

2. Materials and Procedures

2.1. Materials
Conductive composites were prepared with poly(dimethyl siloxane) (Unibond) as the elastic host matrix. Dendritic nickel particles (Johnson Mathey) as shown in Figure 1 were used as the conductive filler. The composites were prepared by manually mixing the filler into the matrix polymer until evenly distributed through the mix. Samples for testing were cast into an open topped mould and left to cure for 24 hours. Sample strips 1mm x 8mm x 60mm were cut from the cross-linked sheet.

![Figure 1. Scanning electron microscope image of the dendritic nickel used in this work.](image)

2.2. Experimental Procedures
A computer controlled tensiometer was used for simultaneously recording the stress-strain data and the conductivity values. Samples were mounted in special clamps that allow four-probe conductivity measurements to be simultaneously taken of the samples as they are being deformed. The strain rate was $\sim 5 \times 10^{-3}$ s$^{-1}$. All measurements were made at room temperature.

3. Results
A series of samples were prepared containing different proportions of the filler particles. It was found that the conductivity of composites containing 10% vol., or more of the nickel particles increases dramatically once a threshold strain is exceeded. An example is shown in Figure 2 for a composite containing 20% w/w of nickel particles having an unstrained conductivity of $(6.8 \pm 0.14) \times 10^{-11}$ S/cm. After a strain of 0.045± 0.005 the conductivity increases by 10 orders of magnitude over a strain range of 0.2. At higher strains, the conductivity tends towards a plateau value. This data has some similarity to the conductivity-concentration plots of percolating systems (Equation 1), however here the concentration of the conductive filler remains constant. Hence the dramatic rise in conductivity typical of the formation of percolative pathways is not due to a changing concentration. Here we propose that the increase in conductivity is due to an increase in electrical contact between particles. When strain is applied, the geometric centres of the particles move apart from each other according to the deformation of the elastomer. Particle protrusions and extremities of particles that are close
enough to be entangled have a chance of becoming in contact as the separation increases with strain. As strain increases, there is an increasing number of contacts, and decreasing resistance of existing contacts, between neighbouring particles and eventually percolative pathways are formed.

It is well established that metal particles usually contain a thin oxide coating which is non-conducting. Indeed, the loose dendritic nickel powder was found to be non-conducting in the absence of applied pressure\(^\text{12}\). One possible explanation of the threshold strain observed in Figure 2 is that such a strain is required to produce sufficient contact pressure to break the oxide layer allowing conductive pathways to be formed. To test this, we coated the dendritic particles with gold as gold only develops a very thin oxide layer on its surface and hence any contact between Au coated particles will be a conducting contact \(\text{[11]}\). The loose gold coated particles were highly conducting in the absence of applied pressure\(^\text{12}\). The resultant strain behaviour of 20% gold coated particles in poly(dimethyl siloxane) is also shown in Figure 2. In the relaxed state this sample has a measurable conductivity. This suggests that at 20% loading of gold coated dendritic nickel particles, there is a percolating network of contacts. In the case of the non-coated particles, however we propose that the contact forces are insufficient to create conducting contacts in the relaxed state. The rapid rise in conductivity at low strains and a plateau level of conductivity at high strains is still present in the 20% gold coated particle sample. This strongly suggests the formation of new contacts with strain that leads to an increasing conductivity with strain. We have developed a quantitative model based on the concept of contact formation which is presented in the next section.

![Figure 2](image-url)  
**Figure 2.** A plot of the conductivity recorded as a function of the strain applied during loading for a conductive composite based on (a) 20% w/w of dendritic nickel and (b) 20% w/w of gold coated dendritic nickel both with a matrix of poly(dimethyl siloxane). The continuous lines represent the predictions of the model developed in this work.

### 4. Model

Dendritic particles have great irregularity of shape. The protrusions and surface distortions lead to a large potential for entanglement and increased contacts. We use the term overlapping to describe these effects. We consider the overlapping by representing the dendritic-particles as spheres of radius \(r\), where \(r\) is the distance from the geometric centre of a dendritic particle. The probability of a volume with a sphere being occupied by the dendritic particle is taken as constant, each particle is rigid and non-deformable and the centres of the spheres move in an affine manner with respect to the deformation of the composite. Any pair of spheres with their centre points located within a distance of \(2r\) will overlap. By considering the geometry of the volume of the overlap we can construct a relationship which describes the concentration of contacts as a function of strain \(\text{[12]}\). The particles are not in electrical contact for zero strain and so we introduce a condition that overlapping regions must have a relative deformation greater than a threshold strain before contacts develop. To compare
this model with the experimental data, it is necessary to determine how the concentration of contacts relates to the conductivity and for this we use Equation 1, where \( p \) is now taken as the concentration of contacts. In this simple model we consider that all particles behave in the same manner and thus as soon as a non-zero fraction of contacts is formed we can assume a sample-spanning cluster of contacts between particles and consequently an increase in conduction; as a consequence the critical concentration of contacts \( (p_c \) in Equation 1) is taken as zero. We have taken the exponent in Equation 1 to be 2, the so-called universal value and the scaling factor is the only adjustable parameter.

We compare the predictions between the model and the experimental data in Figure 2 and there is excellent agreement in terms of the basic behaviour. At higher strain there is a divergence between experiment and model. The model outlined here focuses on forming contacts, while the data suggests the breaking of contacts becomes significant at the highest strains. This model has clear implications for other elastomer composite systems. In systems with highly structured carbon black, this model and the inter-locking mechanism could account for the increase in conductivity with strain at intermediate and higher strains. It is possible that at lower strains, the breaking of established contacts with separation of particles dominates, with the inter-locking mechanism operating at all strains, but dominating at higher strains and causing the commonly observed inversion point as discussed earlier. When this new model is applied to spherical particles, there is no degree of overlap of particles and therefore no increase in contact intensity with strain, as observed, for example [12].

5. Summary
A deformable composite made with dendritic nickel particles and poly(dimethyl silicoane) shows a dramatic increase in conductivity when strained. This increase in conductivity has been attributed to an increase in electrical inter-particle contacts of the highly structured metal particles with strain. The increase in electrical conductivity with strain arises as a consequence of an increasing number of contacts. A model has been developed to describe how the concentration and conductance of contacts, between dendritic particles in a deformable medium increase with applied strain. We observed good agreement between the model and the experimental data.

6. References
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