CONDUCTION AND RESPONSE MECHANISMS IN STRAIN SENSORS BASED ON ELECTRICALLY CONDUCTIVE POLYMER COMPOSITES

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The authors investigate conduction and response mechanisms in strain sensors based on electrically conductive polymer composites. It is found thatsensitivity of the sensor to the applied strain depends on the volume fraction of the conductive filler. Different strain intensities affect conducting paths in therandom conductive network causing the reversible change in resistance, while percolation thresholds and dispersion levels in polymer matrices depend on the material selection.

Keywords: conductive composites, polymers, tunneling, metallic conduction, percolation threshold.

Introduction

Composites are multiphase materials.Their final properties are result of the synergy of the initial constituents. Most of the composite materials consist of two phases, one phase providing the functional properties and the other one providing the shape and structural integrity (matrix phase). Polymers are often used as matrices in conductive composites because they are easily processable materials withwide range of properties. The insulating nature of polymers tends to limit their application range, and so conductive fillers are added to form electrically conductive polymer composites[1—4] suitable for strain sensing applications in health-monitoring, human motion detection, soft robotics, structural health monitoring, etc. [3—5] These strain sensors are resistive-type sensors since their resistance depends on their inner conductivenetworks and the change in resistance is used to detect and measure the applied strain. However, the dispersion state of the conductive filler in the polymer matrix during the preparation process is unpredictable and conductive mechanisms present in the composite are still often discussed. For these reasons this paper focuses onstudying conduction and response mechanisms in strain sensors based on electrically conductive polymer composites.

Conduction in electrically conductive polymer composites

Conduction in electrically conductive polymer composites is not yet fully understood because of the random dispersion of conductive filler in the polymer matrix during the material preparation process. Dispersion state of the filler strongly depends on physicochemical properties of the polymer, as well as the structure and morphology of the filler itself.

Conductive mechanisms present in the electrically conductive polymer composite are directly related to the volume fraction of the conductive filler (Fig. 1). At low volume fractions of the conductive filler, polymer performs as an insulator. At higher volume fractions of the conductive filler, nearing the percolation threshold, random conduction network begins to form causing an increase in conductance. For higher filler volume fractions an efficient conduction network is formed leading to the conductance saturation.

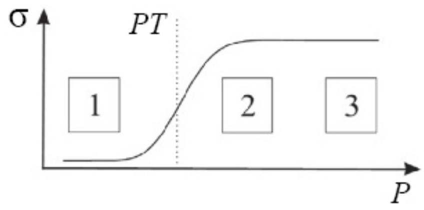

Fig. 1. Conduction of the electrically conductive polymer composite vs volume fraction of the conductive filler:
1 — loading is low and the composite remains insulating;
2 — formation of the conductive network(*PT* — percolation threshold);
3 — conductive polymer composite

Depending on the volume fraction of the filler conducting mechanisms can be grouped into two categories:

— metallic conduction;
— tunnelingthrough thin polymer barriers.

The tunneling barrier model exists in composites with low filler content. During the preparation process, particles of the conductive filler are immersed in the polymer matrix andinsulating barriers between neighboring filler particles are formed. In such cases dominant conduction mechanism is tunneling conduction through thin insulating barriers that can be expressed as [1]:

$$\sigma_t \sim e^{-r/d} \quad (1)$$

where $\sigma_t$is the tunneling conductivity;r is the tunneling distance and d is the tunneling decay parameter.

Tunneling distance depends on the volume fraction of the conductive filler. Higher filler contents lead to the reduction of the tunneling distance and the increase in the conductivity of the composite. At the percolation threshold random conductive network is formed. Some filler particles remain separated by thin polymer barriers, while others form contacts or, for high filler contents, agglomerations in the polymer matrix where metallic conduction becomes dominant (Fig.2).

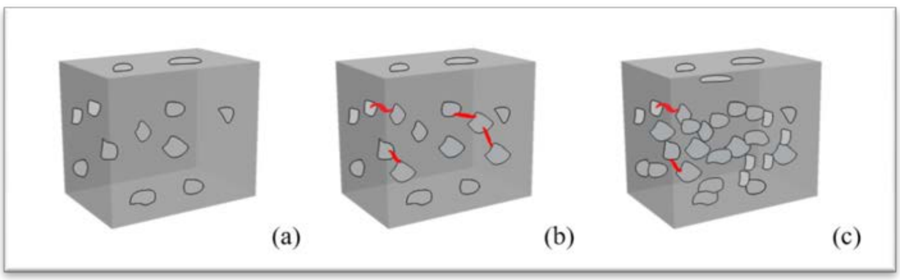

Fig. 2. Conducting mechanisms in electrically conductive polymer composites:
a — conductive filler dispersed in the insulating polymer matrix;
b — with increasing filler content conduction via tunneling occurs (red lines in the schematic drawing);
c — with further increase in filler content conductive paths are formed

When dealing with electrically conductive polymer composites, researchers often use a model based on the percolation theory. This approach offers an explanation for the empirically observed characteristics of composites using their macrostructural characteristics. Conduction mechanisms are not included in the model. For electrically conductive polymer composites, percolation theory is used to describe conductance as the function of the volume fraction of conductive filler [4]:

$$\sigma = \sigma_0 (p - p_c)^t \qquad (2)$$

where σ andσ_0 are conductivities of the composite and conductive filler, respectively, p is the volume fraction of the conductive filler, p_c is the cut-off volume phase of the conductive filler and$t$ is the conductivity index.Cut-off volume phase of the conductive filler is the percolation threshold, a minimum loading of the conductive filler needed to form an electrically percolated conductive network in the polymer matrix.

Response mechanism in strain sensors based on electrically conductive polymer composites

Response mechanisms of strain sensors formed using electrically conductive polymer composites are based on the piezoresistivity effect. Piezoresistivity is the phenomenon that describeschange of resistance upon the application of the external strain. Gage factor is usually used to evaluate the strain sensitivity of the sensing device:

$$GF = \frac{\Delta R}{R_0 \varepsilon} \qquad (3)$$

where ΔR is the relative change in resistance and R resistance of the electrically conductive polymer composite under the applied strain ε.

Sensitivity of the sensor to the applied strain depends on the volume fraction of the conductive filler and, thus, on conducting mechanisms present in the composite.

Small strains in composites with low volume fraction of the filler cause small sensing signals. The most of the particles of the conductive filler are separated by insulating barriers and straining affects tunneling distances between neighboring filler particles causing a small change in resistance.

Higher strains affect both tunneling distances and direct connections between neighboring filler particles breaking conductive paths in the sensor (Fig. 3). This induces larger changes in resistance and therefore sensing signals are stronger. This effect is reversible. After the applied strain is removed, good elasticity of the polymer matrix leads to recovery of the conductive network. However, depending on the conductive network rearrangement that is a result of type and geometric morphology of the conductive filler, type of elastomer and processing technique used, some of the paths may stay disrupted causing the increase in the initial resistance.In that case, if stabilization of the conductive network cannot be achieved by application of cyclic tension or compression, choice of materials should be reconsidered.

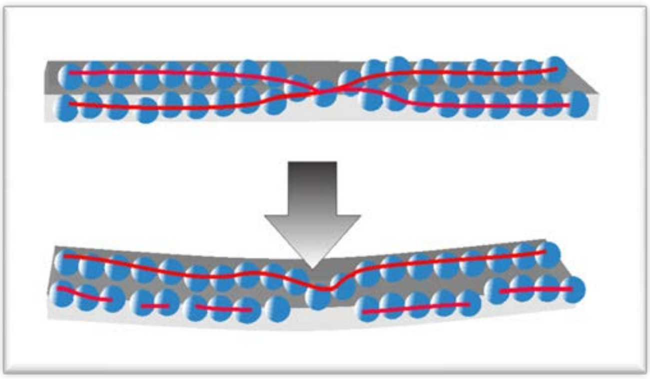

Fig. 3. Higher strains affect both tunneling distances and direct connections between neighboring filler particles breaking conductive paths in the sensor

To produce electrically conductive polymer composites elastomers such as polyurethane (TPU) or polydimethylsiloxane (PDMS) are often used. Carbonaceous fillers, intrinsically conductive polymers and nanometals are commonly used as electrically conductive fillers. List of several commonly used materials and processing techniques is given in the Table.

Commonly used materials and processing techniques for realization of electrically conductive polymer composites

Polymer matrix	Conductive fillers	Processing techniques
polydimethylsiloxane	carbon nanotubes	diffusion process
thermoplastic polyurethane	carbon black	spray-coating
polyurethane	graphene	spin-coating
polypropylene	carbon fiber	dip-coating
rubber	silver nanowires	solution mixing
polyolefin elastomers	silver nanoparticles	in situ polymerization
polycarbonates	gold nanosheets	coagulation/hot pressing
Ecoflex	Cu nanowires	wet spinning

Conclusion

The paper describedconduction and response mechanisms in strain sensors based on electrically conductive polymer composites. It was found thatsensitivity of the sensor to the applied strain depends on the volume fraction of the conductive filler and, thus, on conducting mechanisms present in the composite:metallic conduction and tunneling through thin polymer barriers. Small strains affect tunneling distances between neighboring filler particles causing a small change in resistance. Higher strains affect both tunneling distances and direct connections between neighboring filler particles. Breaking of conductive paths induces larger changes in resistance. Although the effect is reversible, in some cases a number of the paths may stay disrupted causing the increase in the initial resistance.In that case, stabilization of the conductive network must be performed using cyclic tension or compression. Otherwise, choice of materials should be reconsidered in terms of lowering percolation thresholds and increasing dispersion levels in polymer matrices.

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Механізми провідності та відгуку в тензодатчиках на основі електропровідних полімерних композитів

Досліджено механізми електропровідності та відгуку в тензодатчиках на основі електропровідних полімерних композитів. Встановлено, що чутливість датчика до прикладеної деформації залежить від об'ємної частки електропровідного наповнювача. Різна інтенсивність деформації впливає на провідні шляхи у випадковій провідній мережі, викликаючи оборотну зміну опору, тоді як пороги перколяції та рівні дисперсії в полімерних матрицях залежать від вибору матеріалу.

Ключові слова: електропровідні композити, тензодатчики, полімери, тунелювання, металева провідність, поріг перколяції.