Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp645-646

Highly Reproducible Strain Responses of PEDOT:PSS/Polyurethane Elastomeric Composite for Wearable Strain Sensor Applications

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Abstract

Conductive materials which have piezoresistivity in strain range ($\varepsilon > 0.5$) are highly desirable for resistive type strain sensors for wearable sensor applications because of their high sensitivity and broad sensing range. However, the hysteresis of resistance in the sensing material is the major huddle for achieving highly reproducible strain sensor. Rearrangement of conductive fillers inside of resistive material causes significant hysteresis of resistance during the repeated stretching. Here, we demonstrate resistive type strain sensor with low hysteresis by introducing highly porous carbon black into the PEDOT:PSS/Polyurethane composite matrix. The gauge factor of strain sensor was 20.1. And the hysteresis of resistance after experience the high strain ($\varepsilon = 0.5$) was suppressed to 49 times smaller ($\Delta R/R_0$ = from 25.6 to 0.52) than pristine material. Interestingly, SEM images reveal that PEDOT:PSS molecular chains aggregate near the highly porous carbon black. This polymer aggregation near the carbon fillers might be dominant factor for reducing the hysteresis of resistance change.

1. Introduction

Soft materials that can convert mechanical strain into the changes of electrical properties such as resistance, capacitance, and electrical potential have been exploited to realize highly conformable and stretchable physical sensors such as wearable tactile sensors, smart clothing, and artificial skin and prosthetics [1-3]. Resistive type strain sensor which consist of conductive fillers such as metal particles, graphene, carbon nanotubes, conductive polymers embedded in elastomer matrix is one of the promising approaches because of their high gauge factor, simple process and scalable device structures [1]. Especially, poly(3,4-ethylenedioxy thiophene):polystyrene sulfonate (PEDOT:PSS) and polyurethane (PU) composite is a promising candidate for wearable strain sensor applications because of their low young's modulus (7.7 - 250 MPa when it contains 1-25 wt% PEDOT:PSS), solution processability, and printability [4, 5].

However, the hysteresis of resistance is one of the biggest challenges for the practical strain sensor applications. M. Seyedin et al reported the strain responses of conductive elastomeric composite which consists of PEDOT:PSS and polyurethane [5]. It showed high hysteresis mainly because of the relocation of PEDOT:PSS chain networks inside of the PU matrix. Therefore, enabling the reversible change of conductive networks is of key importance to achieve highly reproducible strain responses.

2. Improved reproducibility of strain responses in PEDOT:PSS/PU composite by adding carbon additives

Fabrication process of PEDOT:PSS/PU composite

Water-based polyurethane emulsion (PUE1000, solid content: 49 wt%, Murayama Chem, Japan) was mixed with PEDOT:PSS aqueous solution (PH1000, solid content: 1 wt% Heraeus, Germany) in weight ratio of 2:1. Then, carbon additives (Ketjen black, particle size of 50 nm) was added from 0.1 wt% to 11 wt% and vigorously mixed by planetary centrifugal vacuum mixer. After preparation of the solution, the ink was stencil printed directly on a polyurethane film substrate and a knitted textile substrate, then dried in convection oven at 90 ℃ for 1hr. Figure 1a, b are images of PEDOT:PSS/PU composite film with carbon additives printed on a 20 μm thick polyurethane film and a stretchable knitted textile substrate.

Electrical characteristics of PEDOT:PSS/PU composite during the repeated stretching cycles

To evaluate strain responses of PEDOT:PSS/PU composite with carbon additives, cyclic tensile strain ($\varepsilon = 0.5$) was precisely applied to the composite film by stretching machine (AG-X, Shimadzu, Japan) and resistance was monitored by digital multimeter simultaneously. Moreover, to verify the effect of carbon additives, dynamically changing strain was applied. For the dynamic stretching test, 10 stretching cycles were applied to the composite film with three different strains. $\varepsilon = 0.1$ for 0-50 sec, $\varepsilon = 0.3$ for 50-140 sec, $\varepsilon = 0.5$ for 140-250 sec. And the dynamic stretching test was repeated 3 times.

As shown in Figure 1c, PEDOT:PSS/PU composite with 11 wt% carbon additives shows low hysteresis strain response at high strain ($\varepsilon = 0.5$) during 10 cycles with high sensitivity of which gauge factor is 20.1. On the other hand, PEDOT:PSS/PU composite without carbon additives showed irreversible increment of resistance. Normalized resistance change ($\Delta R/R_0$) at released state was 25.6 (or 2560%) after dynamic stretching test as shown in a Figure 1d, while PEDOT:PSS/PU composite with carbon showed small increment of resistance ($\Delta R/R_0 = 0.52$, or 52%) at released state after the test as shown in Figure 1e. As a result, by introducing carbon additives into PEDOT:PSS/PU composite, hysteresis was suppressed 49 times smaller than composite without carbon additives.

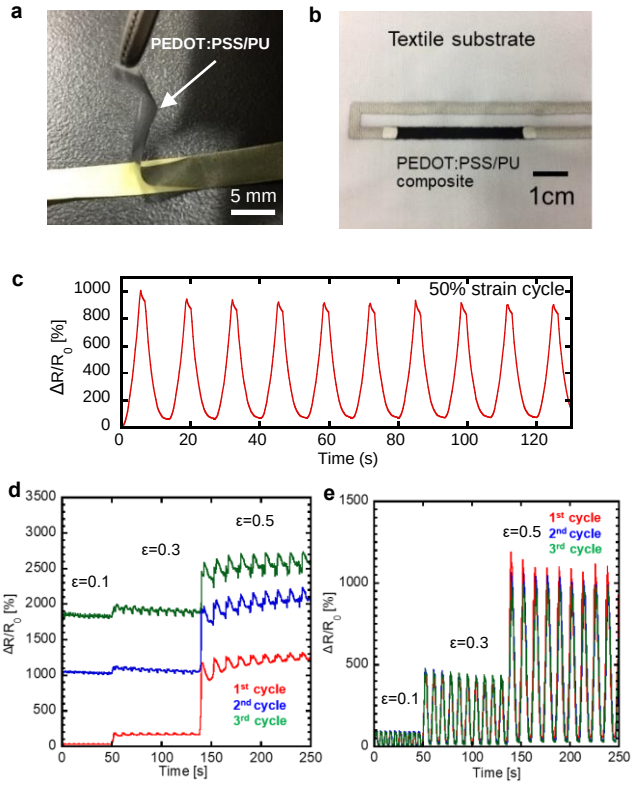

Figure 1. Highly reproducible strain responses of PEDOT:PSS /Polyurethane composite. **a.** PEDOT:PSS/PU composite printed on 20µm polyurethane film. **b.** directly printed on knitted textile substrate for wearable strain sensor. **c.** Normalized resistance change of PEDOT:PSS/PU composite with carbon additives during 10 cycles of 50% strain. **d.** Normalized resistance change of PEDOT:PSS/PU composite without carbon additives during dynamic stretching test. red, blue, green line is first, second, third cycle of the test, respectively. **e.** PEDOT:PSS/PU composite with carbon additives during the dynamic stretching test.

Mechanism of hysteresis reduction

Carbon fillers dispersed in polymer matrix interacts with molecular chain of polymer by forming bound rubber (aggregated polymer) near the interface of carbon and polymer matrix [6]. SEM images reveal that carbon fillers in PEDOT:PSS/PU composite bind the PEDOT:PSS molecular chains together and play a role as fixed points which prevent severe relocation and disconnection of PEDOT:PSS chain networks in the polyurethane matrix. Figure 2a is a surface SEM image of PEDOT:PSS/PU composite without carbon additives. In the image, PEDOT:PSS chains are dispersed in polyurethane matrix and forming random network of conductive paths. Figure 2b is a surface SEM image of PEDOT:PSS/PU composite with carbon additives. Carbon particles aggregated together PEDOT:PSS molecular chains inside of composite material. Figure 2c, d are SEM images of PEDOT:PSS/PU composite with carbon additives before and after stretching 50%, respectively. After stretching the composite film 50%, PEDOT:PSS chain networks start disconnecting as shown in right side of Figure 2d. In contrast, PEDOT:PSS chains near the carbon particles kept their network structures, which would contribute to the reduction of hysteresis.

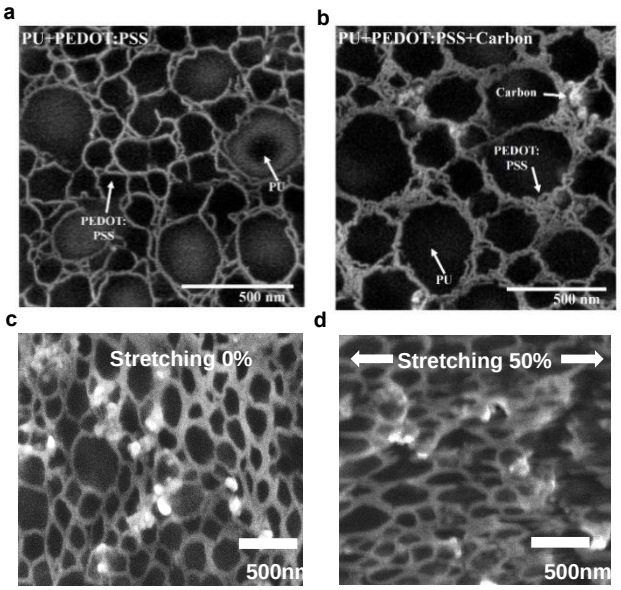

Figure 2. surface SEM images of the PEDOT:PSS/PU composite. **a.** PEDOT:PSS/PU composite without carbon additives, **b.** PEDOT:PSS/PU composite with carbon additives, black circles are PU, grey lines are PEDOT:PSS molecular chains, bright white circles are carbon particles **c.** surface of PEDOT:PSS/PU composite with carbon additives before stretching. and **d.** after stretching up to 50% strain. Scale bars are 500 nm.

3. Conclusions

In this work, we demonstrated significant reduction of hysteresis in PEDOT:PSS/PU elastic composite by introducing high porous carbon black additives. The proposed method can provide a new design opportunity for wearable strain sensor because of its simple printing process, high sensitivity and reproducibility. Further investigations regarding the interactions between carbon and PEDOT:PSS and its electrical and mechanical properties are needed for fine tuning of device performance in the future.

Acknowledgements

This research was supported by Japan Science and Technology Agency (JST) program SICORP, NEC Corporation, and the Center of Innovation Program from Japan Science and Technology Agency, (JST). H. Jin was supported by Graduate Program for Leaders in Life Innovation (GPLLI). The authors appreciate for fruitful discussions with Mr. Mohammad Abbas.

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