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Versatile Poly(3,4-ethylenedioxythiophene) Poly(styrenesulfonate) Films on Polydimethylsiloxane Substrates Having Random Micro Ridges: Study of Resistive Behaviors of a Polymer–Polymer Laminate

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ABSTRACT: Conductive polymers such as poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) or PEDOT:PSS has become increasingly important in present day organic electronics. PEDOT:PSS being a polymer is more durable than metals used in electronics and thus offers greater mechanical flexibility during operation. This article presents results regarding resistive behaviors of blade coated PEDOT:PSS films on polydimethylsiloxane (PDMS) substrate having random micro ridges as a function of axial strain and different temperatures. The average resistance of the blade coated PEDOT:PSS films were found to increase by 1.4 times between 35 and 45% axial strain. The resistances of the films were found to change within the temperature range of 25–230°C without any thermal morphological degradations and the polymer–polymer laminate also showed linear thermal actuation behavior. These results suggest that the blade coated PEDOT:PSS films on PDMS substrates with random micro ridges can be potentially useful in versatile applications like stretchable conductors, thermal actuators, thermoelectric generators, and as heating surfaces. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41235.

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INTRODUCTION

With the advent of organic materials and solution-based inks in electronics industry, more cost-effective and direct methods of device fabrication that can work at atmospheric conditions such as ink-jet printing, electrohydrodynamic printing, roll to plate printing, gravure printing, spin coating, and blade coating are becoming exceedingly valuable and are known as printed electronics.[1–9] The major attraction of printed electronics over conventional techniques like photolithography, physical vapor deposition, and chemical vapor deposition lies in its cost effectiveness, atmospheric processability, and availability of wide material options. Beside these advantages printed electronics also offers mass production capabilities.

Unlike the conventional rigid electronics, stretchable and flexible electronic systems requires that the device must remain operative with minimum electrical degradation when subjected to mechanical loads such as tension (stretching), bending, twisting, and repeated loadings.[5,10,11] In order to introduce this feature in the device two alternatives are employed: (a) intelligent geometrical design of interconnects and (b) the use of intrinsically stretchable and flexible materials. However, it must be noted that the overall performance of the fabricated device heavily depends on the fabrication method employed and therefore is of prime concern.[12] This later fact can also serve to compare various alternatives available for the fabrication of a particular device. Based on this fact versatile poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) films on polydimethylsiloxane (PDMS) substrate having random micro ridges has been fabricated using a cost-effective and non-vacuum blade coating technique, and its resistive behaviors are studied.

PEDOT:PSS is an intrinsically conductive polymer that has been shown to have potential applicability in electronic devices like flexible solar cells, stretchable conductors, organic light emitting diodes, electromechanical actuators, and thermoelectric generators.[5,10,13–15] PEDOT:PSS has also been found to remain chemically stable and soluble with many different solvents which can further improve its conductivity and hence its functionality[16] thereby making it a promising material for organic electronics. On the other hand, PDMS is hydrophobic in nature and therefore poses obstacles in adhering to liquids. To overcome this problem various techniques have been designed which includes, chemical treatment, oxygen plasma exposure, and UV ozone exposure of PDSM surface before using it as a substrate.[17–19] Unlike other techniques texturing of the PDMS surface is a permanent way of increasing the adhesion between the substrate

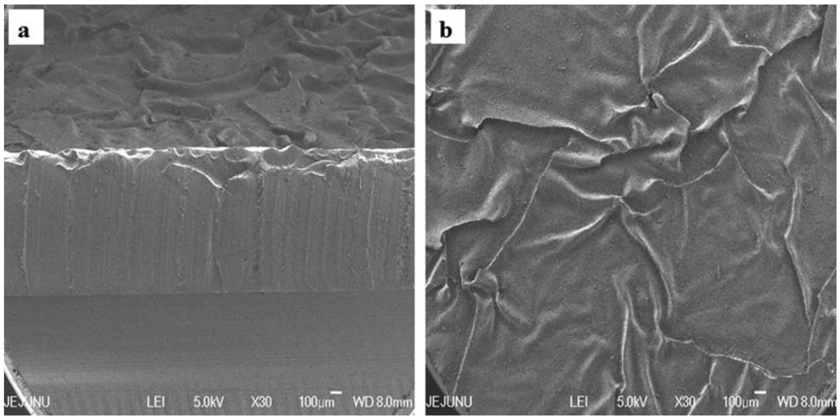

Figure 1. FESEM images of PDMS sample having random micro ridges: (a) lateral view and (b) plan view.

and the deposit since it introduces roughness patterns on the surface of the PDMS which also act as strain relief features.[20–23] Good adhesion between the substrate and the deposited material is found to suppress the delamination due to interfacial shear and hence increases the overall stretchability of the device.[24]

Therefore, this article studies the stretchability and resistive behaviors of blade coated PEDOT:PSS thin films on rough PDMS substrate with random micro ridges. The results are encouraging and suggest that these blade coated PEDOT:PSS films can have versatile applications such as stretchable conductors, thermal actuators, heating surfaces, and thermoelectric generators. Based on the experimental results and past research work simple correlation has been presented to quantify the resistive behaviors of the stretchable polymer–polymer laminate as a function of axial strain.

EXPERIMENTAL

Materials

PDMS was purchased from Dow Corning, South Korea and was prepared by mixing the two components in a 10 : 1 ratio by weight followed by degassing in a vacuum chamber for 20 min. PEDOT:PSS in the form of a thick paste was purchased from AGFA Materials, Japan and was used as received. The relative humidity during all experiments was 35%.

PDMS Substrate and PEDOT:PSS Film Fabrication

The PDMS substrates with random micro ridges were prepared by casting the 10 : 1 liquid PDMS solution against wrinkled aluminum foils having a thickness of 10 µm. The wrinkles were generated by squeezing the aluminum foils by hand and each time carefully unfolding the squeezed foils and then squeezing them back. This procedure is repeated several times (six times) before finally unfolding the foils and suppressing the wrinkles using a soft hammer. The suppression of the wrinkles is necessary since large amplitudes of the wrinkles can severely reduce the stretchability of the PDMS substrates. The PDMS castings were annealed inside a furnace at a temperature of 100°C for 30 min.[25] The PDMS substrates were then cut into dimensions of 20 mm by 5 mm and an approximate thickness of 1 mm. Finally, the PDMS substrate were analyzed using field emission scanning electron microscope (FESEM) images in order to quantify the roughness pattern and a roughness ratio based on the average amplitude of the ridges and the spacing between them was defined.[23] For the PDMS samples used in this study, the roughness ratio was found to be 0.3. A typical SEM image of the PDMS substrate having random micro ridges is shown in Figure 1. PEDOT:PSS paste was applied on these PDMS substrates using the miniaturized blade coating apparatus whose schematic is shown in Figure 2. The blade velocity was kept at 26 mm/sec for all samples prepared in this study. The PEDOT:PSS films were annealed at a temperature of 110°C for 15 min inside a furnace.[26] Figure 3 shows the as fabricated PEDOT:PSS films on PDMS substrates having random micro ridges. Due to the presence of complex roughness patterns the film thickness was measured using gravimetric analysis.[27] The mass of the PDMS substrates were measured with and without the films on a precision mass balance having a least count of 0.01 mg and the thickness was estimated from the definition of the density of the PEDOT:PSS film. The average thickness was found to be 16 µm for these blade coated films.

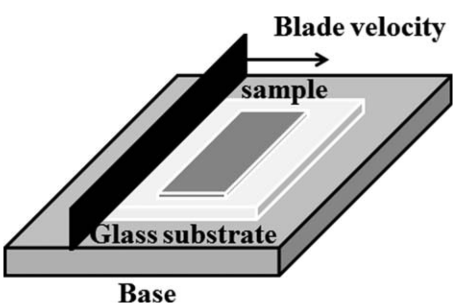

Figure 2. Schematic of the blade coating apparatus.

Resistance Measurements

The as fabricated PEDOT:PSS films were loaded in a home-made stretching apparatus with a resolution of 10 µm. Conductive silver epoxy was used to form electrical connections and was secured by heating on a hot plate at a temperature of 100°C for 10 min. 0.05 mm diameter pure copper wires were used to connect the film with a digital multimeter having an accuracy of 0.8%. The elongations were applied in steps of 30 µm until the films were ruptured and resulted in an open circuit. The entire schematic of the setup is shown in Figure 4. Similar setup was used to measure the resistances within a

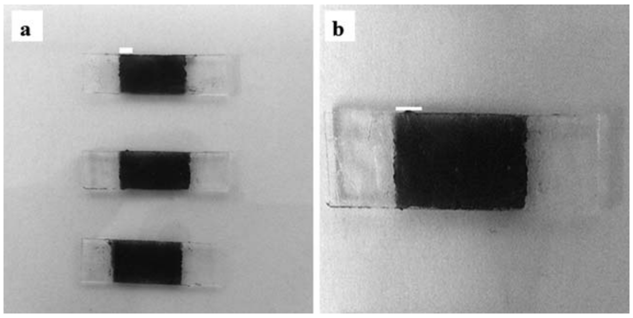

Figure 3. As fabricated PEDOT:PSS films on PDMS substrates having random micro ridges. Scale bar in (a) and (b) is 2 mm.

temperature range of 25–230°C. However, this time the samples were placed on a hot plate and the resistances were measured at different temperatures.

Thermal Actuation Measurements

The sample was placed on a 1-mm thick glass substrate and fixed at one end by applying heat resistant stick tape. The assembly was then placed on a hot plate and actuations were measured using a scale with a resolution of 0.5 mm.

RESULTS AND DISCUSSIONS

Resistive Behavior as a Function of Applied Strain

Figure 5 shows the variation in resistance as a function of axial strain for the as fabricated PEDOT:PSS films on PDMS substrate having random micro ridges for three tested samples (these samples were not in any case different from each other and were fabricated by following the same experimental protocols, however, specially at higher strains the difference in the resistive behavior among these samples is attributed toward the high randomness of the roughness patterns used in this study which also effect the crack evolution). From this figure it can be seen that the films remain conductive even at an average strain of 78%, however, with an increase in the value of resistance that is on average 19 times higher than the initial resistance (unstretched condition). As shown in Figure 6, the cracks can appear as a brittle fracture and are due to tensile stresses in the film,[24,28] which tend to split the films into two halves. However, as mentioned earlier, the reason why these films remains conductive even after crack formation is due to the presence of random micro ridges on the surface of the PDMS substrate which tends to increase the adhesion, suppresses the crack propagation, and allows the films to remain conductive even after cracking by forming random interconnected bridges (links).

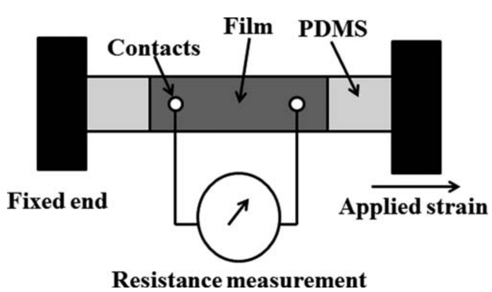

Figure 4. Schematic of the resistance measurement set up.

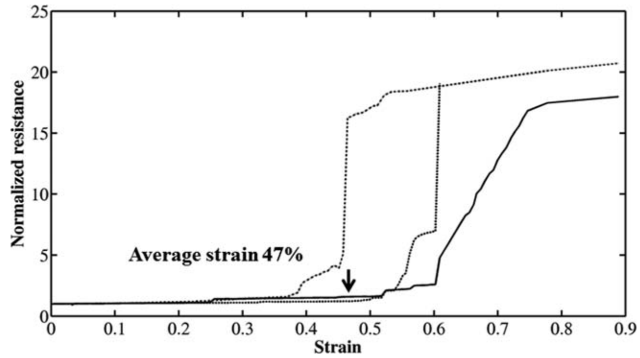

Figure 5. Normalized resistance vs. strain for the as fabricated PEDOT:PSS films on PDMS substrates having random micro ridges (to represent statistical consistency result for three samples is shown).

This behavior indicates the usefulness of the random micro ridges on the PDMS surface and could possibly open a door way for further optimization in topographic designs of these interconnected micro features for various applications. On the other hand, from Figure 5 it can be realized that on average up to 45% axial strain, the increase in the value of the resistance as compared to the initial value, remains below 1.5; therefore, this range can be considered as the useful stretchable range for these blade coated PEDOT:PSS films on PDMS substrates having random micro ridges. Figure 7 shows the increase in the resistance of the films up to 35% axial strain. This curve represents an average taken over three tested samples. It can also be seen that a theoretical model[22] seems to fit this variation with a coefficient of determination of 0.74 while a proposed second degree polynomial fits the experimental data points with a much better value of 0.96. A quantitative investigation into the resistive behavior of these films with respect to the applied strain suggests that the change in resistance actually depends on the geometric part more dominantly than the piezoresistive part ($K = -0.22$) where K is the piezo component neglecting any dimensional changes along the thickness direction and can be calculated using Figure 5 and the Poisson ratio of

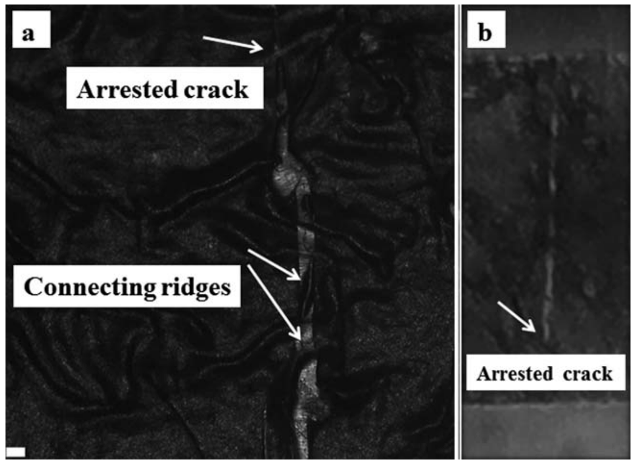

Figure 6. A typical crack propagation behavior of as fabricated PEDOT:PSS film on PDMS substrate having random micro ridges: (a) Micrograph and (b) photographic image. Scale bar in (a) is 50 μm.

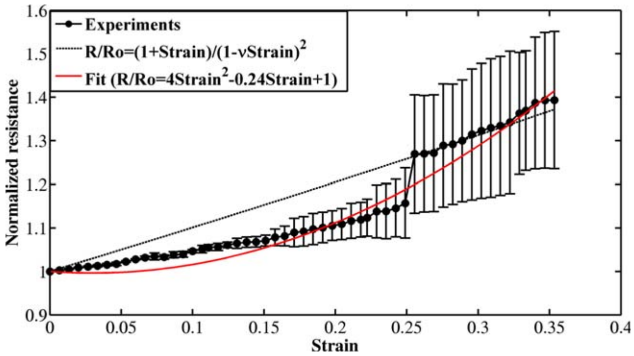

Figure 7. Average normalized resistance vs. strain for as fabricated PEDOT:PSS films on PDMS having random micro ridges for three tested samples. Error bars show the standard deviation from the mean value of the normalized resistance at each value of strain. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PEDOT:PSS.[29] Consequently, these films breaks with a brittle crack formation near the critical value of the strain as mentioned earlier. This ultimately indicates that the morphological changes within the films remain minimal during stretching and contribute in a way that reduces the resistance changes, as indicated by a negative sign until cracking appears and begins to propagate. Finally it can be concluded that for the as fabricated PEDOT:PSS films on PDMS having random micro ridges, the useful range of stretchability lies between 35 and 45%. This behavior suggests that the as fabricated films can be used as stretchable conductors in applications like stretchable electronics.

Resistive Behavior as a Function of Temperature

There exist several experimental studies which have demonstrated the resistive behavior of PEDOT:PSS films on polymeric substrates as a function of temperature,[30–32] however, the results seems to depend on factors such as temperature range, thickness of the films, morphology, and experimental conditions. Most studies have suggested increase in the resistance of the PEDOT:PSS films between the temperature range of 20–100°C. However, PEDOT:PSS being a polymer exhibits decrease in its resistance due to increased tunneling effect with increasing temperatures.[33] The temperature range used in our study could be increased due to high thermal stability of PDMS as a substrate

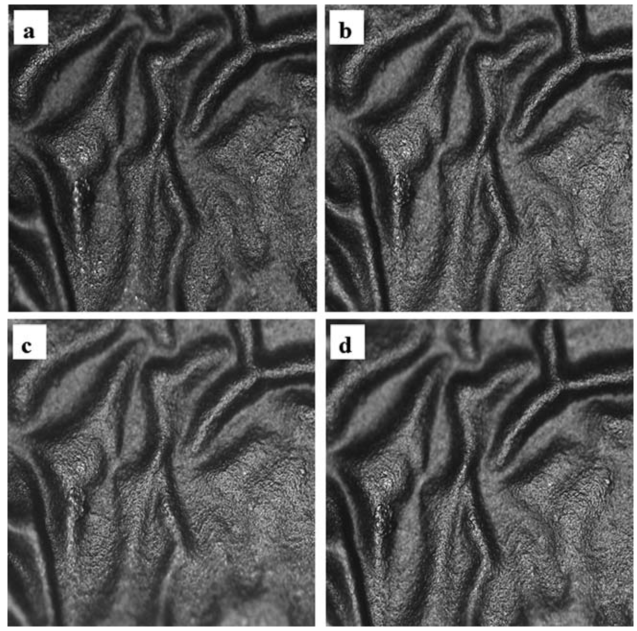

Figure 9. Micrographs of PEDOT : PSS film at different temperatures (a) 25°C, (b) 150°C, (c) 230°C, and (d) 25°C.

material and therefore lie between 25 and 230°C. Figure 8 depicts the resistive behaviors of three samples. It can be noticed that each sample shows increase in the resistance up to an average temperature of 80°C and thereafter starts to decrease. This decrease in resistance indicates an increase in the intermolecular hopping which is due to thermally assisted tunneling effect.[30] It can be seen that for the as fabricated PEDOT:PSS films the tunneling effect can be triggered within 80–100°C. Also in the temperature range of 25–100°C the average increase in the resistance was only 1.14 times the initial resistance and on the other hand the resistance decreases by almost two times within the temperature range of 100–230°C. Further it can be seen from Figure 9 that even at a temperature of 230°C no thermal morphological degradations has taken place which indicates thermal stability of these PEDOT:PSS films on PDMS substrates having random micro ridges. This

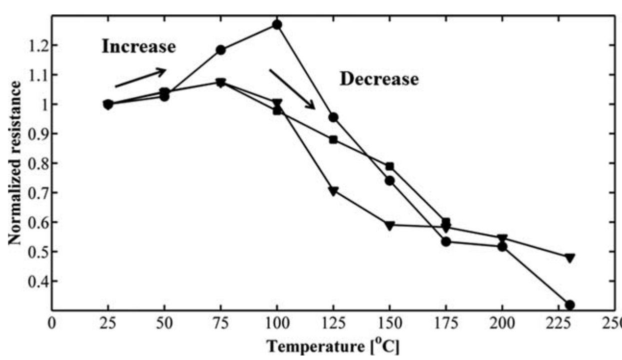

Figure 8. Normalized resistance vs. temperature for PEDOT : PSS films on PDMS having random micro ridges for three tested samples.

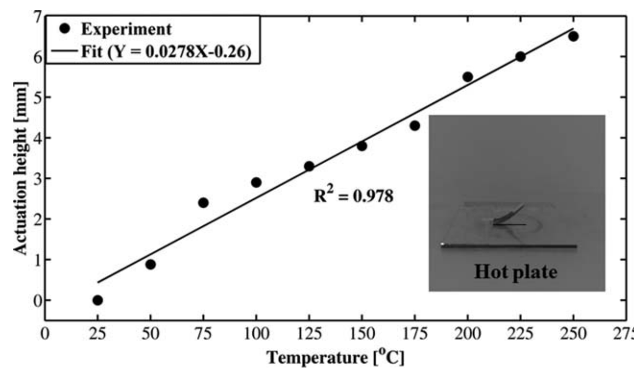

Figure 10. Thermal actuation behavior of a typical PEDOT : PSS film on PDMS substrate having random micro ridges. The inset shows a photographic image of the actuator. The scale bar is 1 mm.

behavior is encouraging in the sense that this polymer–polymer laminate can be used as heating surface in microfluidics applications and also as thermoelectric generators.

Thermal Actuation Behavior

Figure 10 shows the actuation behavior of the blade coated PEDOT:PSS films on PDMS substrate having random micro ridges. It can be seen that the as fabricated polymer–polymer laminate shows a good linear thermal actuation behavior. The actuations were in orders of millimeters with response time of 2.4 sec per degree rise in temperature. When the sample was removed from the hot plate it fully recovered its initial horizontal position in less than a minute. The behavior suggests that the polymer–polymer laminate can also be used as a thermal actuator or thermal valve in microelectromechanical systems and microfluidics applications.

CONCLUSIONS

Cost-effective and non-vacuum blade coating method was applied to fabricate the PEDOT:PSS films on PDMS substrate having random micro ridges. The useful stretchability of the as fabricated polymer–polymer laminate was found to lie between 35 and 45% axial strain which is due to the presence of random micro ridges that increases the adhesion and stretchability of the blade coated films. Within this range of axial strain the electrical resistance only increases by 1.4 times the initial value. A quadratic model is presented that relates the increase in resistances with the applied strain for the as fabricated polymer–polymer laminates. These PEDOT:PSS films show thermal stability at high temperatures (up to 230°C) without any thermal degradation and show increased tunneling effect at increasingly high temperatures (on average beyond a value of 80°C). The polymer–polymer laminate was also found to show good linear thermal actuation behavior. The blade coated PEDOT:PSS films on PDMS substrates having random micro ridges is shown to have versatile applications such as stretchable conductors, thermal heaters, thermoelectric generator, and thermal actuators and therefore, can be potentially useful in applications like stretchable electronics, microelectromechanical systems, and microfluidics applications.

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