

Microstructured Conducting Polymer Coatings on Plastic Strip for Contact Electrodes: Formulation and Tuning of Sheet Resistance

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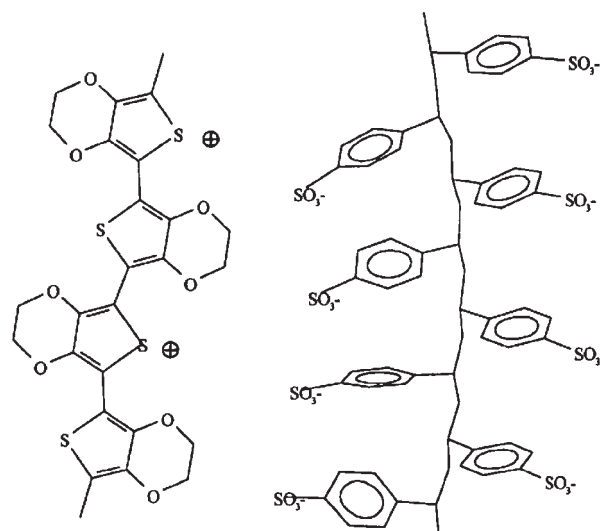
ABSTRACT: Mechanically strong and flexible strips of cellulose acetate were used to support a thin coating of poly(3,4-ethylenedioxythiophene) : poly(styrene sulfonic acid) PEDOT : PSS, an intrinsically conducting polymer (ICP), formulated with an aqueous dispersion of judiciously chosen copolymer of vinyl acetate and ethylene (VAE), to impart adhesion of the coating onto the substrate. Incorporation of a few drops of an organic acid to the formulation resulted in a substantial reduction of the sheet resistance of the coated surface. When the coated strips were post-treated with a salt solution, a fur-

ther fine tuning of the sheet resistance by a factor of 10 was achieved. The coated strips combine high conductivity with flexibility and mechanical strength. The performance of the coated strips has been evaluated in relationship to composition, coating thickness, and sheet resistance for application as contact electrodes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 234–237, 2007

Key words: intrinsically conducting polymer ICP; PEDOT : PSS; formulation; solution processing

INTRODUCTION

An organic polymer that possesses the electrical, electronic, magnetic, and optical properties of a metal or semiconductor while retaining the processibility commonly associated with a conventional polymer is termed an “intrinsically conducting polymer” ICP, more commonly known as “synthetic metal.”¹ ICPs have been the subject of much interest not only from fundamental scientific interest but also from a practical viewpoint for numerous functional applications,^{2–6} including, antistatic and magnetic coatings, thin solid films, sensors and actuators, ion exchange materials, molecular devices and modified electrodes. Within the class of ICPs, a polythiophene derivative poly(3,4-ethylenedioxythiophene) (PEDOT) occupies a unique place. It is environmentally stable^{7,8} and has been functionalized to facilitate solution processing in a variety of solvents.⁹ It is rendered soluble in water by using poly(styrene-sulfonic acid) PSS, a water soluble polyelectrolyte, as a charge balancing dopant during polymerization to yield an aqueous dispersion of PEDOT : PSS. This combination was developed extensively by researchers at Bayer AG, in the second half of the 1980s. The chemical structure of PEDOT : PSS¹⁰ is given below:



Salient structural feature of PEDOT : PSS

PEDOT : PSS is an organic polymer with extensive conjugation in the main chain structure of PEDOT [doped form], that presents electronic conduction. Furthermore, the counter-ion is in excess with respect to the positively charged PEDOT chain. This combination yields an aqueous dispersion with unique advantages including good thermal stability,¹¹ high conductivity,¹² and excellent film formability.¹³ Notable limitations that hinder the use of PEDOT : PSS as a flexible electrode material include the following:

1. Free standing films cast from PEDOT : PSS exhibit weak mechanical properties.

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TABLE I
Characteristic Properties of PEDOT/PSS

Sample	Particle Size (μm)	Solids (%)	Density (g/cc)	Viscosity (mPa/s)	pH
PEDOT/PSS	0.08–1.0	1.2–1.4	1.003	60–100	1.5–2.5

2. PEDOT : PSS coatings exhibit poor adhesion on plastics, attributed to the extensive conjugation in the main chain structure of the PEDOT component resulting in increased chain stiffness and exfoliation of the coating.
3. The coated strips require a lower sheet resistance for the targeted application as a flexible contact electrode.

This study was undertaken to provide a new conducting polymer formulation deposited as a thin coating on plastic strips in an attempt to overcome the aforementioned problems and to provide flexible strips that combine high conductivity with flexibility and mechanical strength for application as contact electrodes¹⁴ with a device designed¹⁵ for early detection of caries by measuring the electrical resistance of the tooth surface.

MATERIALS

PEDOT : PSS (Baytron P), was obtained as an aqueous dispersion from Bayer, Germany. Characteristic properties of PEDOT : PSS are shown in Table I.

The copolymers used in the formulation were provided by Clariant, Germany. Characteristic properties of the copolymer, a nonplasticised aqueous dispersion based on vinyl acetate and ethylene are shown in Table II.

METHOD

Two types of conducting polymer blends were formulated:

- Type I—PEDOT : PSS/copolymer blend
- Type II—PEDOT : PSS/additive/copolymer blends.

Tables III and IV represent the specific recipes for each of these blends and relevant properties.

The Type 1 blends were formed by mixing an aqueous dispersion of PEDOT : PSS with either copolymer 1 or 2 using a mortar and pestle to obtain a homogeneous blend. A known quantity of the resulting blend was cast onto cellulose acetate plastic strips (obtained from Associated Dental Products, Wiltshire, UK), with a syringe to obtain a uniform coating. After casting, the substrates were cured overnight at room temperature in a fumehood. The procedure was repeated for Type II blends except that the aqueous dispersion of PEDOT : PSS was mixed first with a few drops of formic acid (96%, Aldrich) and then with the copolymer to obtain a homogeneous blend. The coated strips for both Type I and Type II blends were then weighed to determine the conductive polymer content. The thickness of the coatings was then evaluated using a vernier.

Each modified substrate of the Type I and Type II blends was treated with about 0.1M magnesium sulfate dissolved in aqueous formic acid (1 : 1 volume ratio), for about 4 h. The treated substrates were then rinsed successively with water to remove excess salt, ethanol and acetone, and finally kept in an air oven at 40°C until the substrates were completely dry.

Surface resistivity of the substrates was measured using a four-point probe technique at various locations on each substrate. The test results for copolymer 1 and 2 are shown in Tables III and IV respectively.

DISCUSSION

PEDOT : PSS is obtained initially as an aqueous dispersion. In this dispersion, PEDOT, the charge transporting species is in its oxidized state, that is, doped form. The counter-ion PSS is in excess with respect to the positively charged PEDOT chain. The ratio of PEDOT : PSS is about 1 : 2.5. This leads to the formation of a nonstoichiometric soluble polyelectrolyte complex¹⁶ defined by the PSS random coil with PEDOT chains ionically linked alongside and the area between the grains consisting of neutral PSS. When

TABLE II
Characteristic Properties of the Copolymer Vinylacetate and Ethylene

Sample	Particle Size (μm)	Solids (%)	Density (g/cc)	Viscosity (mPa/s)	pH
Copolymer1	0.3–1.2	55	1.06	2500	4.25
Copolymer2	0.3–3.0	55	–	14000	4.25

TABLE III
Resistivity Values for PEDOT/PSS: Copolymer 1 Blends

Blend	Sample	Composition, wt (g)			Thickness (mm)	Resistivity (k Ω /sq.)	
		ICP	Additive	Copolymer 1		Untreated	Treated
Type I	1	0.3	–	0.018	0.02	320	–
Type I	2	0.45	–	0.018	0.03	238	–
Type I	3	0.6	–	0.018	0.04	170	–
Type II	4	0.4	0.05	0.02	0.02	2.3	1.0
Type II	5	0.6	0.05	0.02	0.04	8.0	1.2
Type II	6	0.6	0.05	0.018	0.04	5.0	–
Type II	7	0.6	0.05	0.016	0.04	3.0	0.5

the dispersion is cast onto the substrate, a thin polymer film is formed characterized by a nonhomogeneous distribution of PEDOT and PSS species within the conducting grains surrounded by a nonconductive PSS shell.¹⁷ This illustrates the key role played by granularity in the conduction of conjugated polymers.^{18,19} Incorporation of a small quantity of VAE copolymer to PEDOT : PSS adds a nonconducting barrier which increases the surface resistivity of the deposited films as observed in Tables III and IV for the Type I blends. Alternatively, when PEDOT : PSS was mixed first with a few drops of formic acid and then with the VAE copolymer, as in the case of Type II blends, a dramatic decrease in resistivity of the deposited films by a factor of over 200 was observed when compared to Type 1 blends. This indicates the particularly significant role of formic acid as an organic liquid additive in enhancing conductivity of the deposited films. In a related study,²⁰ chemical treatment of the deposited films in acid solution showed a strong increase in conductivity, but the structure of the polymer was not affected by the treatment. This increase in conductivity is explained by the assumption that polar liquid additives induce segregation between PEDOT : PSS and the excess free PSS,²¹ thus allowing better pathways to conduction. Such treatment procedures leading to enhancement of conductivity have been demonstrated previously²² in the case of doped polyaniline employing low molecular weight alcohols and ketones. Tables III and IV also show that when the coated strips of Type II blends

were post-treated with magnesium salt in an aqueous organic acid, a further fine tuning of resistivity by a factor of 10 was achieved. The coated strips made of Type II blends combine high conductivity with good flexibility and mechanical strength. Tensile tests carried out on the strips indicate no exfoliation of the coated layer even at break point. This was further confirmed by the 'cross-hatch' test for evaluating adhesion strength.²³ The adhesion level was 5B in case of all the treated films indicating that none of the squares of the lattice is detached when pressure sensitive tape is applied over the lattice and then removed.

CONCLUSION

This investigation reports the formulation of new conducting polymer coatings deposited on plastic strip for application as flexible electrodes. The conducting polymer PEDOT : PSS was formulated with an aqueous dispersion of selected grades of vinyl acetate and ethylene to impart adhesion of the coating onto the substrate. Incorporation of an organic acid as a liquid additive to the formulation resulted in a substantial reduction in sheet resistivity of the coated surface. Furthermore when the coated strips were post-treated with a salt solution, a further fine tuning of resistivity by a factor of 10 was achieved. The coated strips combine high conductivity with flexibility and strength for a wide range of applications such as inexpensive plastic electronics and transparent flexible electrodes.

TABLE IV
Resistivity Values for PEDOT/PSS: Copolymer 2 Blends

Blend	Sample	Composition, wt (g)			Thickness (mm)	Resistivity (k Ω /sq.)	
		ICP	Additive	Copolymer 2		Untreated	Treated
Type I	1	0.45	–	0.018	0.03	238	–
Type II	2	0.45	0.04	0.018	0.03	10	0.3
Type II	3	0.45	0.08	0.018	0.03	4.6	–
Type II	4	0.45	0.05	0.024	0.03	7.6	–
Type II	5	0.45	0.05	0.009	0.03	8.1	0.34
Type II	6	0.45	0.05	0.016	0.03	8.4	0.17

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