

## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Instruments

#### 3.1.1 Materials

The materials used in this experiment are given below. The manufacturer, molecular formula, molecular weight, the CAS number, and some properties are given for each chemical. CAS stands for Chemical Abstracts Service, an organization that indexes information published in Chemical Abstracts by the American Chemical Society and that provides index guides by which information about particular substances may be located in the abstracts.

##### *3.1.1.1 Ethylenedioxythiophene (EDOT)*

The EDOT used in the experiments was obtained from Aldrich and is sold under the name 2,3-Dihydrothieno[3,4-b]-1,4-dioxin. Its molecular formula is  $C_6H_6O_2S$  and molecular weight is 142.18 g/mol. The CAS number for EDOT is 126213-50-1. EDOT is a liquid monomer and has a boiling point of 193 ° C at atmospheric pressure.

##### *3.1.1.2 Poly(styrene sulfonic acid) (PSS)*

Poly(styrene sulfonic acid) in sodium salt form is manufactured by Aldrich. PSS has a molecular formula of  $[-CH_2CH(C_6H_4)SO_3Na-]_n$  and has a molecular weight of 125,000 g/mol. The CAS number for PSS is 25704-18-1. PSS is a polymer manufactured in power form.

### 3.1.1.3 Sodium Persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ )

The Sodium persulfate that was used in our experiments is manufactured by Aldrich. The molecular formula of sodium persulfate is  $\text{Na}_2\text{S}_2\text{O}_8$ , and it has a molecular weight of 238.1 g/mol. The CAS number for sodium persulfate is 7775-27-1. The sodium persulfate comes in solid form and it soluble in aqueous solution at room temperature.

### 3.1.2 Instruments

A Fourier Transform Infrared Spectrometer (Thermo Nicolet, Nexus 670) with number of scans of 32, A UV-Visible absorption spectrometer (Perkin Elmer, Lambda 10), Thermalgravimetric analyzer (DuPont, model TGA 2950) with the temperature scan from 30 to 900°C with a heating rate of 10°C/min under  $\text{O}_2$  atmosphere were used to characterize the synthesized PEDOT/PSS and PEDOT/PSS/EG blends. Scanning electron microscope (JOEL, model JSM-5200-2AE) was used to determine the morphological structure of the synthesized polymers and polymer blends with the magnifications of 100 and 1000 times at 15 kV. Crystallinity was measured by an XRD (Phillips PW 1830/00 NO. DY1240 Diffractometer, model Rigaku). A custom-built two-point probe electrometer (Keithley, Model 6517A) was used to measure electrical conductivity of the conductive polymer. A melt rheometer (Rheometric Scientific, ARES) was used to measure electrorheological properties. A DC power supply (Instek, GFG 8216A), was used to deliver electric field strength upto 2 kV/mm.

## 3.2 Experimental Methods

### 3.2.1 Polymerization Procedure

PEDOT/PSS was prepared by mixing 3,4-ethylenedioxythiophene (10.65 g, 75 mmol), 439 g of 5.99 wt% PSS solution and  $\text{Na}_2\text{S}_2\text{O}_8$  (21.4 g, 104 mmol) in water (2062 ml). After initial stirring at room temperature for 10 minutes,  $\text{Fe}_2(\text{SO}_4)_3$  (187 mg) was added and the mixture was stirred vigorously for 24 hrs. After this period the dark, aqueous PEDOT/PSS mixture was purified by ion exchanging with Lewatit M600 and Lewatit S100, resulting in dark blue, aqueous PEDOT/PSS. A nice, transparent film of PEDOT/PSS was obtained by casting the aqueous PEDOT/PSS at 100°C for 24 hrs.

### 3.2.2 Secondary Doping of PEDOT/PSS by EG Treatment

The synthesized PEDOT/PSS and ethylene glycol (EG) were mixed by the volume ratio 5:1, 5:2, 5:3, 5:4 and 5:5 (PEDOT/PSS : EG). The mixed solution of PEDOT/PSS and EG was filtered and stirred continuously for 24 hrs at room temperature. After this period, the PEDOT/PSS/EG particles were prepared by casting the solution on glass substrates. The samples were dried in an oven at 100°C for 24 hrs.

### 3.2.3 Preparation of the PDMS PEDOT/PSS Blends

The PEDOT/PSS/EG powder was sieved with a mesh particle size of 38  $\mu\text{m}$  and dried at room temperature for 24 hours prior to their uses. The blends were prepared by mechanical blending of synthesized PEDOT/PSS/EG particle at various particle concentrations (5, 10, 15 and 20vol%) with PDMS. PDMS fluid and a specific amount of crosslinking agent were added to the mixture, which was then mechanically blended for about 5 min to disperse the ingredients. This experiment operated at the crosslinking ratio of 15%. The specific amount of particle was then added and the mixture was mechanically bended for 1 min to disperse the particles. The mixture was

cast on the mold (diameter 25 mm) and bubbles were removed under a vacuum atmosphere at 25°C for 30 min

### 3.2.5 Characterization and Testing

#### 3.2.5.1 *Fourier-Transform Infrared Spectrometer (FT-IR)*

Undoped and doped PEDOT/PSS powder was identified functional groups by a FT-IR spectrometer (Thermo Nicolet, Nexus 670) that operated in the absorption mode with 32 scans and a resolution of  $\pm 4 \text{ cm}^{-1}$ , covering a wavenumber range of 4000-400  $\text{cm}^{-1}$ . Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized PEDOT/PSS was mixed with dried KBr at a ratio of PEDOT/PSS:KBr = 1:20 and molded into pellets under the pressure of 6 tons.

#### 3.2.5.2 *Thermogravimetric Analysis (TGA)*

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to investigate thermal property of PEDOT/PSS and second doped PEDOT/PSS. Polymer powder was loaded into an aluminum pan and operated at temperature scan from 30 to 900°C with a heating rate of 10°C/min under air condition.

#### 3.2.5.3 *Scanning Electron Microscope (SEM)*

Scanning electron micrographs were taken with a JEOL, model JSM-5200 scanning electron microscope to determine the morphology of PEDOT/PSS and PEDOT/PSS/EG in powder forms. Sample powder was placed and taped by a carbon tape on a stub. Before measuring, sample surface was coated with gold by using JFC-1100E ion-sputtering device for 4 seconds. The scanning electron micrographs of samples were taken.

#### 3.2.5.4 X-ray Diffraction Spectroscopy (XRD)

Crystallinity and structure of PEDOT/PSS and PEDOT/PSS/EG powder were identified by the x-ray diffractometer (Rigaku model). Sample powder was packed on a glass plate and measured with  $2\theta = 2-90^\circ$ .

#### 3.2.5.5 Conductivity Measurement: Two-Point Probe Meter

Electrical conductivity is the inversion of specific resistivity ( $\rho$ ) which indicates the ability of material to transport electrical charge. The meter consists of two probes, making contact on a surface of film sample. These probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The applied voltage was plotted versus the current change to determine the linear ohmic regime of each sample. The applied voltage and the current change in the linear ohmic regime were converted to the electrical conductivity of polymer using equation (3.1) as follow:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{1}{K \times V \times t} \quad (3.1)$$

where  $\sigma$  is specific conductivity (S/cm),  $\rho$  is specific resistivity ( $\Omega \cdot \text{cm}$ ),  $R_s$  is sheet resistivity ( $\Omega$ ),  $I$  is measure current (A),  $K$  is geometric correction factor,  $V$  is applied voltage (voltage drop) (V), and  $t$  is pellet thickness (cm).

The geometrical correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing and was determined by using standard materials where specific resistivity values were known; we used silicon wafer chips ( $\text{SiO}_2$ ). In our case, the sheet resistivity was measured by using

the two-point probe and then the geometric correction factor was calculated by equation (3.2) as follow:

$$K = \frac{\rho}{R \times t} = \frac{I \times \rho}{V \times t} \quad (3.2)$$

where K is geometric correction factor,  $\rho$  is known resistivity of standard silicon wafer ( $\Omega \cdot \text{cm}$ ), t is film thickness (cm), R is film resistance ( $\Omega$ ), and I is measure current (A).

#### 3.2.5.6 *Electrorheological Properties Measurement*

A melt rheometer (Rheometric Scientific, ARES) was used to measure rheological properties. It is fitted with a custom-built copper parallel plates fixture (diameter of 25 mm). A DC voltage was applied with a DC power supply (Instek, GFG 8216A), which can deliver electric field strength to 2 kV/mm. A digital multimeter was used to monitor voltage input. In these experiments, the oscillatory shear strain was applied and the dynamic moduli ( $G'$  and  $G''$ ) were measured as functions of frequency and electric field strength. Strain sweep tests were first carried out to determine the suitable strain to measure  $G'$  and  $G''$  in the linear viscoelastic regime. The appropriate strain was determined to be 3% for pure PDMS; PDMS\_PEDOT/PSS and PDMS\_PEDOT/PSS/EG gels. Then frequency sweep tests were carried out to measure  $G'$  and  $G''$  of each sample as functions of frequency. The deformation frequency was varied from 0.1 to 100 rad/s. Prior to each measurement, each pure PDMS and PDMS\_PEDOT/PSS blends samples were presheared at a low frequency (0.039811 rad/s), and then the electric field was applied for 10 minutes to ensure the formation of equilibrium polarization before each measurement was taken. Each measurement was carried out at the temperature of 27°C and repeated at least two or three times.