

CHAPTER III

EXPERIMENTAL

3.1 Materials

Aniline, C_6H_7N (AR grade, Merck) was vacuum-distilled and used as the monomer. Ammonium peroxydisulphate, $(NH_4)_2S_2O_8$ (AR grade, Merck) was used as the oxidant. 38 % Hydrochloric acid, HCl (AR grade, Labscan); 25 % solution of ammonia, NH_4OH (Ar grade, Merck) and methanol, CH_3OH (AR grade, Labscan) were used as received. The base fluids, silicone oil (AR grade, Dow corning) with density 0.96 g/cm^3 and kinematic viscosities of 100, 500 and 1000 cSt were vacuum-dried and stored in a desiccator prior to use. Poly(dimethylsiloxane), hydroxy terminated, $HO-[Si(CH_3)_2O]_n-H$ (viscosity 3,500 cSt, Aldrich) was used as a precursor of the cross-linked elastomeric matrix. Tetraethyl orthosilicate (TEOS), $Si(OC_2H_5)_4$ (AR grade, Aldrich) and Dibutyltin dilaurate (2EHSn), $CH_3[(CH_2)_{10}CO_2]_2Sn[(CH_2)_3CH_3]_2$ (AR grade, Aldrich) were used as a crosslinking agent and a catalyst, respectively.

3.2 Polymerization Procedure

PANI was synthesized via an oxidative coupling polymerization according to the method of Cao *et al.*(1989). 20.4 g of distilled aniline was added to 250 ml of 1.5M HCl and the mixture was vigorously stirred and cooled to $0-5\text{ }^\circ\text{C}$ in a 3-necked round bottom flask. 250 ml of 1.5M HCl solution containing 25.5 g $(NH_4)_2S_2O_8$ was then added dropwise to the flask within an hour. After the total amount of the oxidant had been added, the reaction mixture was stirred at $0-5\text{ }^\circ\text{C}$ for 4 hours. The precipitated PANI was recovered from the polymerization flask, filtered and then washed with distilled water until the washing liquid was completely colorless. To remove oligomers and other organic byproducts, the precipitate was washed with methanol several times until the methanol solution was colorless. The precipitate was then dedoped by immersion in 3% NH_4OH , washed until the washing liquid was

neutral, and subsequently dried at room temperature for 48 hours in a vacuum oven, until its electrical conductivity no longer depends on drying time, before being passed through a 38 μm sieve shaker to control the particle size and its distribution. In order to increase its conductivity, the emeraldine base was then suspended in a solution of CSA in water for 24 hrs at 40°C. The doping level was controlled by fixing the molar ratio $N_{\text{CSA}}/N_{\text{EB}}$ at 5 (Koul *et al.*, 2000).

3.3 Preparation of ER fluids

Prior to mixing in silicone oil, PANI powder was dried for 2 days at room temperature to remove moisture in a vacuum oven at room temperature. The particles were then dispersed in the silicone oil with an ultrasonicator for 30 minutes at 25 °C. The PANI suspensions were then prepared at various volume fractions. They were stored in a dessiccator and redispersed by ultrasonification for a period of 10 minutes at 25 °C before each experiment.

3.4 Preparation of PANI/PDMS composites

PANI/PDMS composite specimens were prepared by blending PANI particles with HO-PDMS and TEOS at a crosslinking agent to monomer ratio (C/M) of 0.053, using 2EHSn as the catalyst. The mixtures were poured in a mold and allowed to cure under vacuum for 24 hrs.

3.5 Characterization Methods

Fourier transform infrared spectroscopy (FT-IR, Bruker, Equinox 55/FRA 1065) was used to confirm the chemical structure of PANI. The spectrometer was operated in the transmission mode averaging 32 scans at a resolution of $\pm 4 \text{ cm}^{-1}$, covering a wavenumber range of 400-4000 cm^{-1} using a deuterated triglycine sulfate

detector. Optical grade KBr (Carlo Erba Reagent) was used as a background material. The samples were ground with KBr and pressed to form pellets.

Ultra Violet-Visible-near Infrared Spectra were recorded with a UV spectrometer (UV-Vis, Shimadzu, UV2550) using deuterium as the light source and a slit width of 2.0 nm. The spectra were recorded in the wavelength range between 300-900 nm at a scan speed of 240 nm/min.

Thermogravimetric analysis (TGA) data was performed using a thermogravimetric differential thermal analyzer (RIS Diamond TG-DTA, High Temp 11), at a heating rate of 10 °C/min, under nitrogen, from 30 °C to 750 °C.

The particle size distribution of PANI powder was determined by a particle size analyzer (Malvern, Master Sizer X).

Scanning electron microscopy (SEM, JEOL, JSM-5200-2AE) was used at an acceleration voltage of 10 kV and a magnification of 350 to investigate the morphology of PANI particles. Prior to observation, samples were gold sputtered.

3.6 Specific Conductivity Measurement

To determine the electrical conductivity, PANI powder was pressed into disk pellets by a hydraulic press (diameter of 25 mm and ~0.2 mm thick). Electrical conductivity was measured using a custom-built four-point probe at 30 °C. The measurements were performed in the linear Ohmic regime where the specific conductivity values are independent of the applied DC voltage.

3.7 Electrorheological Properties Measurement

3.7.1 Electrorheological Properties Measurement under Oscillatory Shear

Dynamic rheological properties of the suspensions were investigated using a controlled-strain fluids rheometer (ARES, Rheometric Scientific Inc.) with a custom-built copper parallel plate geometry (diameter of 50 mm) attached to insulating spacers which are connected to the transducer or motor. The electric field for ER measurement was applied using a high voltage power supply (Source Meter,

Keithley 2410). The voltage amplitude could be precisely controlled in the range of 0-1 kV corresponding to an electric field $E = 0-2$ kV/mm. The electric field was applied for 10 minutes to obtain an equilibrium fibrillar or columnar structure before each measurement was taken. The samples were first tested for viscoelastic linearity by strain sweep mode tests. The resulting stress was decomposed into in-phase and out-of-phase contributions, the storage and loss moduli, G' and G'' . The experiments were carried out in the frequency sweep mode with frequency (ω) ranging from 0.1 to 100 rad/s at a temperature of 25 ± 1 °C to investigate the effect of electric field strength on G' and G'' . The experiments were repeated at least two or three times for each applied electric field strength to ensure reproducibility.

3.7.2 Electrorheological Properties Measurement under Steady Shear

Rheological properties were carried out using a rotational rheometer (Carrimed, CR50) with 4 cm diameter parallel plate geometry at 25 ± 0.1 °C. The gap for the geometry used was 0.2 mm for each measurement. A DC voltage was applied during the rheological measurements using a high voltage power supply (Bertan Associates Inc., Model 215). The electric field was applied for 10 minutes to ensure the formation of equilibrium agglomerate structure before a measurement was taken. The static yield stress was measured using the controlled shear stress mode (CSS) as the highest stress value prior to the onset of flow in the presence of an electric field of specified magnitude. CSS experiments were also applied to investigate the dependence of viscosity on shear stress above the yield point. In the CSS experiments, the shear sweep was always applied at a sweep rate of 40 Pa/min. The temporal response of the suspension was also studied in the time sweep mode during which the electric field was turned on and turned off successively with the frequency ω fixed at 10 rad/s. The experiments were repeated at least two or three times for each applied electric field strength to ensure reproducibility.

3.7.3 Creep and Recovery Behaviors Measurement

The creep and recovery behaviors were carried out using a stress-controlled rheometer (Carrimed, CR50) with 4 cm diameter parallel plate geometry at 25 ± 0.1 °C. The gap for the geometry used was 0.2 mm for each measurement. A DC voltage was applied during the measurements using a high voltage power supply

(Bertan Associates Inc., Model 215). For the initial conditioning, the suspensions were subjected to a steady shearing at 300 s^{-1} for 120s and then the flow was stopped before the electric field was applied for 10 minutes to obtain an equilibrium fibrillar or columnar structure before each measurement was taken. A constant stress was then instantaneously applied, maintained for 200 s, and then suddenly removed. The quasi equilibrium values of strain were measured at $t = 200\text{s}$ as functions of concentration, electric field strength, and temperature.

3.8 Morphological Observation

The morphology of the PTAA particles was characterized using scanning electron microscopy (JEOL, JSM-5200-2AE), using an acceleration voltage of 20 kV and a magnification of 1,000. The formation of particle chain structures in the electric field under stationary conditions was observed with an optical microscope (B&B Microscopes, Ltd., Olympus BX60) equipped with a camera (Diagnostic Instrument Inc., model # 3.2.0). ER fluids were placed between stationary thin copper foil electrodes attached to glass slides. External electric fields were applied to the suspensions using a DC power supply (Source Meter, Keithley 2410).