

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

Silica particles of two types, S5631, and Hisil 927 (Sigma/ -Siam Silica Co., Ltd.) were used in the preparation of particle dispersed ER fluids.

Aniline monomer (Merck) was distilled before used as the starting material for synthesizing polyaniline and polyaniline-coated silica. Ammonium peroxy sulfate (Merck) was used as an oxidant.

Silicone oil, used as a medium for preparing ER fluid samples, was supplied by Dow Corning (Thailand) Ltd. and used as received. The kinematic viscosity is 100 cSt and the specific gravity is 0.960 at 25°C.

#### 3.2 Methodology

##### 3.2.1 Purification of Aniline Monomer

Aniline monomer was purified according to the method of Perrin *et al.* (1985). 100 ml of aniline monomer was dried with 0.25 grams of calcium hydride (CaH<sub>2</sub>), for 30 minute. The dried aniline was twice distilled in reduced pressure at 60°C. The colorless of aniline was obtained and stored in nitrogen atmosphere at 0°C prior to use.

##### 3.2.2 Synthesis of Polyaniline Particles

In this work, polyaniline particles were synthesized through chemical oxidative polymerization suggested by Leclerc *et al.* (1989). 0.5 mol of aniline was added into 300 ml of 1 M HCl solution and was cooled to 5°C in an ice bath. The prechilled solution of 0.5 mol ammonium peroxy sulfate in

100 ml of 1 M HCl was added dropwise to the reaction system with a continuous stirring for 0.5 hour. After that, the conditions were maintained for 2 hours for a complete reaction. Then the polyaniline particles were dedoped by suspending them in a pH8.5 aqueous medium of  $\text{NH}_4\text{OH}$  and HCl to obtain polyaniline in a semiconducting form. The polyaniline particles were filtered and washed with distilled water, ethanol, and cyclohexane respectively in order to remove excess monomer and oligomer and to make sure that the surface of the particle is hydrophobic for better wetting between particle and medium. Finally, polyaniline particles were dried in a vacuum oven at room temperature for 1 day to obtain a fine green powder and kept in a decicator prior to use.

### 3.2.3 Synthesis of Polyaniline-Coated Silica Particles

Polyaniline-coated silica particles were prepared by chemical oxidative polymerization with various amounts of aniline monomer in the presence of silica particles as Kuramoto *et al.* (1994) suggested. Aniline monomer and 1 g of silica particles were added into 300 ml of 1 M HCl solution and was cooled to 5°C in an ice bath. The prechilled solution of 0.5 mol ammonium peroxy sulfate in 100 ml of 1 M HCl was added dropwise to the reaction system with a continuous stirring for 0.5 hour. After that, the conditions were maintained for 2 hours for a complete reaction. Then the polyaniline coated silica particles were dedoped by suspending them in a pH 8.5 aqueous medium of  $\text{NH}_4\text{OH}$  and HCl. The polyaniline particles were filtered and washed with distilled water, ethanol, and cyclohexane respectively. Finally, polyaniline coated silica particles were dried in a vacuum oven at room temperature for 1 day and kept in a decicator prior to use.

### 3.3 Characterizations

#### 3.3.1 Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectra were obtained from a FT-IR spectrometer (Bruker, FRA106/S), in order to identify important functional groups of the silica particles and the synthesized polyaniline and the polyaniline-coated silica particles. The FTIR experiments were done in a transmission mode with 16 scans at a resolution of  $8\text{ cm}^{-1}$ . The wavenumber range was  $4000\text{-}400\text{ cm}^{-1}$ , using a deuterated triglycine sulfate detector (DTGS) with a specific detectivity,  $D^*$ , of  $1 \times 10^4\text{ cmHz}^{1/2}\text{ W}^{-1}$ . Optical grade KBr (Carlo Erba Reagent) was used as the background material. The KBr was pressed hydraulically into a pellet and quickly taken to the FTIR chamber. The KBr spectra background was collected with 16 scans and a resolution of 4%. After obtaining the background spectra, the sample was then mixed with dried KBr at an approximate ratio of sample: KBr = 1:20, then ground and transferred to the sample holder using the same procedure as mentioned above.

#### 3.3.2 Ultraviolet-Visible Spectrometer (UV-VIS)

Ultraviolet-visible spectra were recorded with an UV-VIS Spectrometer (Perkin-Elmer, model Lambda 10), in order to observe the absorption wavelengths of the quinoid and benzenoid units of the emeraldine base. The experiments were done with a scan speed of  $240.00\text{ nm/min}$  and with the slit width of  $2.00\text{ nm}$ . A deuterium lamp was used as the light source. Polyaniline was dissolved by *n*-methyl-2-pyrrolidone (NMP) and put into a glass cell. The sample solution was viewed microscopically for centering and aperturing to a chamber; the transmission light was passed through the sample to record the light transmission as a function of wavelength in the range between  $300\text{-}900\text{ nm}$ .

### 3.3.3 Scanning Electron Microscope (SEM)

Scanning electron micrographs were taken out to determine the morphology of silica, polyaniline, and polyaniline-coated silica particles. SEM digitized photographs were obtained from JOEL Scanning Electron Microscope (model 5200 – 2AE), with a magnification range of 35-200,000 times.

Each sample was stickled on a brass-stub by using an adhesive tape and the surface of the sample was coated with a thin Au film, produced by a vacuum evaporation. The sample was placed into the specimen stage inside the microscope then the pictures were collected by using acceleration voltages between 5-20 kV with magnifications between 750-2000 times.

### 3.3.4 Thermogravimetric Analyzer (TGA)

In order to determine the decomposition temperature and water content of silica, polyaniline, and polyaniline-coated silica particles, thermogravimetric analysis, (Du Pont, model TGA 2950) was carried out. 10-20 mg of each sample was loaded in to a Pt pan and heated from 50°C to 750°C at a heating rate of 20°C under N<sub>2</sub> using a flow rate of 20 ml/min.

### 3.3.5 Particle Size Analyzer

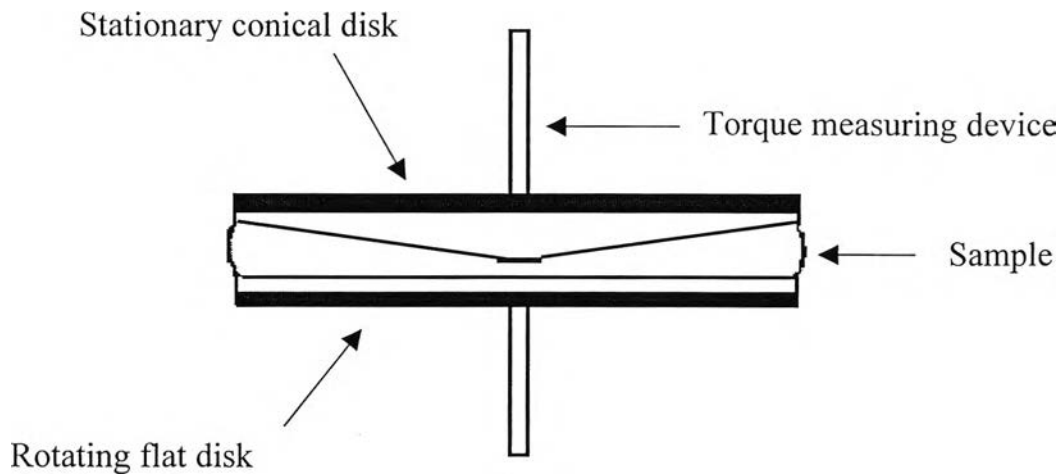
Particle size distribution of silica, polyaniline, and polyaniline-coated silica particles were determined by the particle size analyzer (Malvern, Mastersizer X). The appropriate concentration was adjusted by adding the particles slowly, little at a time, allowing time for the sample to mixed through the system, and then observing from the obscuration value (10-40 %). A suitable measurement time was 10 to 30 seconds depending on the size distribution.

### 3.3.6 Sieving Machine

The broad size distribution sample was sieved through 38 and 53 micron sieves by a Restch sieving machine in order to obtain a narrower size distribution.

### 3.3.7 Fluid Rheometer

A fluid rheometer ( Rheometric Scientific Inc., model ARES), was used to measure rheological properties of the ER fluid suspensions in steady state, strain sweep, and oscillatory modes. It is a strain controlled instrument; the base system consists of a test station, the power chassis, and the host computer. In this work, a modified cone-and-plate fixture was designed and fabricated; it has a diameter of 50 mm, a cone angle  $0.0396^\circ$  and gap size 0.063 mm (see Appendix A). This apparatus consists of 2 circular disk, a stationary upper plate and an oscillating lower plate, made from copper connected to a voltage generator. Each sample was placed between these 2 plates. The bottom plate was oscillated at a frequency with a specified strain while the top plate was held stationary and the torque was measured by a transducer. Torque can be converted to shear stress and other viscoelastic properties such as storage modulus, loss modulus, tangent, etc.



**Figure 3.1** Schematic diagram showing the principal features of cone-and-plate.

#### A. Shear strain rate

For a constant rotational speed  $N$  rpm, the linear velocity ( $v = \omega r$ ) is  $2\pi r N / 60$  cm/sec, where  $\omega$  is the angular velocity (rad/sec) and  $r$  is the radial position in centimeters. Then gap height at  $r$  is  $r \tan \theta_0$  where  $\theta_0$  is the cone angle. Hence, the shear strain rate (1/sec) at a given  $r$  can be written as

$$\dot{\gamma} = \frac{2\pi N}{60r \tan \theta_0} = \frac{\pi N}{30 \tan \theta_0} \approx \frac{\pi N}{30\theta_0} \quad (3.1)$$

Because the cone angle is always maintained to be very small, the approximation of  $\tan \theta_0 = \theta_0$  does hold.

#### B. Shear Stress

The following expression defines the relationship between the measured torque,  $T$ , and the shear stress,  $\tau_{21}$ :

$$T = 2\pi\tau_{21} \int_0^R r^2 dr = \frac{2}{3}\pi\bar{R}^3\tau_{21} \quad (3.2)$$

Thus,

$$\tau_{21} = \frac{3T}{2\pi\bar{R}^3} \quad (3.3)$$

The shear stress is then obtained in dyn/cm<sup>3</sup> when T is expressed in dyn/cm and  $\bar{R}$  is the radius of plate in cm. The ratio of Eq. (3.3) to Eq. (3.1) results in the apparent viscosity, expressed in Poise.

#### C. Normal Stress Difference

The cone-and-plate configuration can be used for estimating the primary normal stress difference of the sample. If  $\bar{p}$  is the pressure at the point on the plate in excess of that due to the atmosphere pressure, then it can be shown that the total normal force  $N_F$  on the plate is given by

$$N_F = \int_0^R 2\pi r \bar{p} dr \quad (3.4)$$

Upon integration gives

$$N_F = \frac{\pi\bar{R}^2}{2} N_1 \quad (3.5)$$

Thus,

$$N_1 = \frac{2N_F}{\pi\bar{R}^2} \quad (3.6)$$

Using Eq. (3.1) and (3.6), a plot of the primary normal stress versus shear rate can be generated. The shear stress and primary normal stress measurements

can be made simultaneously on the sample when it is subjected to unidirectional rotation shear in the gap of cone-n-plate viscometer.

#### D. Oscillatory Shear

The cone-n-plate viscometer can be used for oscillatory shear measurements as well. In this case, the sample is deformed by an oscillating driver, which may be mechanical or electromagnetic. The amplitude of the sinusoidal deformation by the small deformation of a relatively rigid spring or tension bar to which a stress transducer is attached. Because of the energy dissipated by the viscoelastic polymer, a phase difference develops between the stress and the strain. The complex viscosity behavior is determined from the amplitudes of the stress and strain and the phase angle between them. The results are usually interpreted in terms of the material functions  $\eta'$ ,  $G'$ ,  $G''$ , and others.

### 3.4 Preparation of ER Fluids

#### 3.4.1 Preparation of Silica Dispersion System

ER fluid samples were prepared by dispersing silica (Sigma, and Hisil927) particles in silicone oil by 5, 10, 20 and 40 wt% as shown in **Table 1a**. All ER fluids were prepared by dispersion with an ultrasonicator for 30 minutes at 25°C. The prepared ER fluids were kept in a desiccator prior to use, and redispersed before each experiment.

**Table 1a** Preparation of silica dispersion ER fluid

| Silica type | Conc. (wt%)   | Medium       |
|-------------|---------------|--------------|
| Sigma       | 5, 10, 20, 40 | Silicone oil |
| Hisil 927   | 5, 10, 20, 40 | Silicone oil |



### 3.4.2 Preparation of Polyaniline Dispersion System

ER fluids based on polyaniline particles were prepared by dispersing polyaniline particles in silicone oil by 5, 10, 20 and 40 wt% as shown in Table 1b. All samples were prepared by dispersion with an ultrasonicator for 30 minutes at 25°C. The prepared ER fluids were kept in a desiccator prior to use, and redispersed before each experiment.

**Table 1b** Preparation of polyaniline dispersion ER fluid

| Particle type | Conc. (wt%)   | Medium       |
|---------------|---------------|--------------|
| PAN           | 5, 10, 20, 40 | Silicone oil |

### 3.4.3 Preparation of Polyaniline-Coated Silica Dispersion System

ER fluids based on polyaniline-coated silica particles were prepared by dispersing these particles in silicone oil by 5, 10, 20 and 40 wt% as shown in Table 1c. All samples were prepared by dispersion with an ultrasonicator for 30 minutes at 25°C. The prepared ER fluids were kept in a desiccator prior to use, and redispersed before each experiment.

**Table 1c** Preparation of polyaniline-coated silica dispersion ER fluid

| Particle type | Amount of aniline monomer (mol/l) | Conc. (wt%)   | Medium       |
|---------------|-----------------------------------|---------------|--------------|
| PAN-sigma     | 20                                | 5, 10, 20, 40 | Silicone oil |

### 3.5 ER Measurements

An electric field was applied for five minutes in order to obtain equilibrium chainlike or columnar structure before applying the shear. All measurements were performed at  $25 \pm 0.1^\circ\text{C}$ . In order to obtain reproducible data, the ER fluid was redispersed before each experiment, and measurements were carried out at least two or three times.

#### 3.5.1 Conditions in Oscillatory Measurement

##### 1) Dynamic strain sweep default test

Usually, the rheological properties of viscoelastic material are independent of strain up to a critical strain. Beyond this critical strain level, the material behavior is nonlinear and the moduli decline. Thus, measurement of the strain amplitude dependence of the storage and loss moduli was the first step taken in characterizing the viscoelastic behavior. A strain sweep test was used to establish the extent of the linearity of the viscoelastic response of a material.

The measurements were performed by an ARES Rheometer using the cone-n-plate geometry with a cone angle of  $0.0396^\circ$  and a diameter of 50 mm. The gap range was  $0.065 \pm 1$  mm. The experiments were carried out at the frequency of 0.05 rad/s, at the temperature of  $25 \pm 1^\circ\text{C}$ . The initial strain and the final strain were equal to 0.1 and 100%, respectively. For these measurements, the level of strain was determined in order to ensure that all measurements were made within the linear viscoelastic regime.

##### 2) Dynamic frequency sweep default test

After the fluid linear viscoelastic regime has been established by the strain sweep test, its structure can be further characterized using a frequency sweep at a strain below the critical strain. This provides more information about rheological properties at difference length on time scales. In the dynamic frequency sweep mode, measurements were made over

a range of oscillation frequency at a constant oscillation amplitude and temperature.

The measurements were performed by an ARES Rheometer using the cone-n-plate geometry with a cone angle of  $0.0396^\circ$  and a diameter of 50 mm. The gap range was  $0.065 \pm 1$  mm. The experiments were carried out at the temperature of  $25 \pm 1^\circ\text{C}$ . The initial frequency and the final frequency were equal to 100 and 0.01 %, respectively. The value of strain used was chosen to be within the linear viscoelastic regime. In these measurements,  $G', G'', \eta'$  were determined as a function of frequency.