# CHAPTER III
# EXPERIMENTAL SECTION

## 3.1 Materials

γ-Methacryloxypropyltrimethoxysilane (γ-MPS) was supplied by Siam Fiberglass Industries Co., Ltd. Fumed silica (AEROSIL 300), surface area 300±30 $m^2/g$, average primary particle size 7 nm, pH value 3.6-4.3 and refractive index 1.45, was purchased from JJ Degussa (Thailand) Co., Ltd. Methylmethacrylate monomer (MMA), water content of 0.05% and a propanol (inhibitor) content of 20 ppm, refractive index 1.4117-1.4125, was supplied by Siam Chemical Industry Co., Ltd. Dodecylamine was purchased from Merck Co., Ltd. Oleic acid was supplied by Imperial Industrial Chemicals (Thailand) Co., Ltd. TSK standard polystyrene, $\overline{M}_w$ = 418, 456, 500 and 2,630, were purchased from Tosoh Corporation. Benzoyl peroxide, 1wt%, was added to the composite for curing. All chemical reagents were used as received.

## 3.2 Instruments and Equipments

### 3.2.1 Brookfield Viscometer

Brookfield viscometer model RVDV-III, with a small sample adapter (SSA 21/13R) and a water bath, was used to measure the viscosity of the mixture. The measurement was performed at 30 °C by controlling the temperature in the water bath. Brookfield viscosity standard (polydimethylsiloxane, η = 4.94 Pa.s at 25 °C) was used for calibration.

3.2.2 Size Exclusion Chromatography (SEC)

Waters GPC 600E was used to qualitatively and quantitatively analyze the γ-MPS hydrolyzates and the unreacted γ-MPS. The temperature of column was 35 °C. The column series consisted of Waters Styragel HR 0.5 and HR 1 column. Tetrahydrofuran (HPLC grade) was used as the mobile phase at the elution flow rate of 1 mL/min. The calibration curve was created by a series of polystyrene standard ($\overline{M}_w$ = 418, 456, 500 and 2,630). The UV detector was used at 254 nm.

3.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

Diffuse reflectance Fourier transform infrared (DRIFT) measurements were performed on a VECTOR 22 Bruker Spectrometer with a hemispherical diffuse reflectance attachment. A deuterated triglycine sulfate (DTGS) detector was used. The spectra were collected at a resolution of 4 $cm^{-1}$ and coaddition of 64 scans. Single-beam reflectance of samples was ratioed against that of the KBr powder and the Kubelka-Munk (KM) function was calculated. The KM function (Eq. 3.1) has the following form:

$$F(R_\infty) = ( 1 - R_\infty )^2 / 2 R_\infty \qquad \text{(Eq.3.1)}$$

where $F(R_\infty)$ represents a ratio between absorption and scattering coefficients and $R_\infty$ is the experimentally measured reflectance spectrum from a semi-infinite specimen.

DRIFT technique was used to quantitatively analyze the relative amount of chemisorbed silane on fumed silica surface. The sample preparation was done by grinding the treated silica and KBr with the agate mortar and grinder.

3.2.4 Torsion Rectangular Rheometer

Advanced Rheometric Expansion System (ARES) with torsion rectangular geometry and the 0.85 mm inserts was applied to analyze the rheological properties of composite. The measurements were done in the temperature scan mode at 1 Hz from 40 °C to 140 °C. The applied strain was within linear viscoelastic region for every sample.

3.2.5 High Speed Refrigerated Centrifuge

Sorvall Super T21 High Speed Refrigerated Centrifuge was used to separate the treated silica from the liquid matrix. The centrifuge tubes were the PPCO type and were used at a controlled temperature of 20 °C.

## 3.3 Preparation of Dodecylammonium Oleate

The catalyst solution was freshly prepared by mixing dodecylammonium oleate, a stoichiometric mixture of dodecylamine and oleic acid. Methylmethacylate was used as a diluent with the ratio of 1:10 by weight. The catalyst solution was stirred by a magnetic stirrer for 5 minutes before use.

## 3.4 Preparation of Fumed Silica Filled MMA Consisting of γ-MPS

### 3.4.1 Study on the Effect of the Amount of γ-MPS

A certain amount of fumed silica (9 g) was dispersed in MMA (141 g) and stirred in round bottom flask. The silane was added into the system with varying the amount from 0.2 to a monolayer equivalence. An appropriated amount of catalyst, dodecylammonium oleate, was also. The monolayer equivalence can be calculated by Eq. 3.1.

The amount of silane monolayer equivalence (g)

$$= \frac{\text{surface area of silica} \times 10^{20} \times \text{molecular weight of silane}}{6.02 \times 10^{23} \times \text{surface area of silane}}$$

$$= \frac{300\,(\text{m}^2/\text{g}) \times 10^{20} \times 248}{6.02 \times 10^{23} \times 50\,(\text{Å}^2)}$$

$$= 0.2472 \text{ g of silane/g of silica} \qquad \text{(Eq.3.1)}$$

The mixture was stirred. The viscosity was measured as a function of time until it became constant. The fumed silica filled MMA was centrifuged by high speed refrigurated centrifuge at 20 °C, 10,000 rpm for 1 h. The supernatant solution was separated and analyzed by SEC to quantify the untreated γ-MPS. The separated silica was dried in vacuum at room temperature for 6 h to remove trace amount of MMA and unreacted γ-MPS.

The obtained silica (1.0 g) was stirred wash with THF (15 mL) by for 2 h to remove the physisorbed silane. After stirring, the solution was centrifuged and the supernatant THF was analyzed for the amount of physisorbed silane. The separated treated silica was dried in vacuum at room temperature for 6 h.

3.4.2 Study on the Effect of the Silica Content

A varied amount of silica, MMA, γ-MPS and catalyst were mixed so that the silica content becomes of 10%, 20%, 30%. The calculated amounts are shown in Table I. The prepared mixture was divided into parts for mixing procedures. Silica, γ-MPS and catalyst were added partially and stirred until the viscosity was constant before adding another part. Other procedures were the same to that described in 3.4.1.

**Table I Variation of Silica Content and the Composition of the Prepared Mixture**

| Silica content / Weight (g) | 10% | 20% | 30% |
|---|---|---|---|
| Silica | 15.00 | 31.00 | 45.00 |
| MMA | 135.00 | 120.00 | 105.00 |
| γ-MPS | 3.7215 | 7.4760 | 11.1645 |
| Catalyst | 3.7443 | 7.8888 | 11.2353 |

## 3.5 Preparation of the Torsion Sample for Rheometric Measurement

The samples were prepared by adding 1wt% of benzoyl peroxide into the treated silica/MMA mixture, then pre-polymerizing at 85-90 °C for 30 min in the closed system and polymerizing in an oven at 50 °C for 5 h in petri-dish. The torsion samples were 30.0 mm long, 8.0 mm wide, and 1.2 mm thick.

## 3.6 Measurements

### 3.6.1 Viscosity Measurement

After pouring the 8 mL sample into the sample chamber, the sample was left until the sample temperature reached 25 °C. The sample was measured at 100 rpm.

### 3.6.2 Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFT)

The treated silica and KBr were weighed and transferred into the agate mortar by ratio of 2:100, and ground well. The prepared mixture was weighed and tranfered to the sample cup. The quantitative analysis was achieved by measuring the area under C=O peak. The C=O band in γ-MPS has a large specific absorptivity, allowing for high-sensitivity measurements. The C=O band also provide information with respect to the amount of the adsorbed silane molecules. The presence of water generates a problem that must be corrected by digital subtraction. The spectrum , was then, fitting by Gaussian and Laurentzian equations under the region 2140 to 1540 $cm^{-1}$ with software. The area of the C=O band was taken from the sum of area under the bands at 1700 and 1710 $cm^{-1}$. Each of the peak area was calculated by normalizing to the concentration of treated silica in KBr (g/g). Peak area was evaluated as a relative amount by using internal thickness band of siloxane group which appeared as a combination band at 1867 $cm^{-1}$.

### 3.6.3 Size Exclusion Chromatography (SEC)

Samples of both unreacted silane and physisorbed silane were examined by SEC. The sample solution was filtered by 0.22 μm PTFE filter before analyzed by SEC. The sample injection volume was held constant at 60

μL. The injected sample concentration was 50wt% in THF for physisorbed silane, and 3wt% in THF for unreacted silane. The area under the peak of physisorbed silane species was integrated to be the relative total amount of physisorbed silane. Each of the peaks was calculated by normalizing to the concentration of sample in THF (g/g).

3.6.4 Rheometric Measurement

For each sample, the first measurement was dynamic strain sweep default test. The strain was varied between 0.001-0.5 rad./sec with a frequency of 1 rad./sec at temperature of 40 °C. The sampling rate was 5 point per decade. The next measurement mode was dynamic temperature step default test. The temperature ranges used were 40-80 °C, 80-120 °C, and 120-140 °C. The temperature increment was 3 °C with a soaking of 180 s for the range 40-80 °C and 300 s for the rest. The value of tan δ versus temperature was collected.