

CHAPTER II

EXPERIMENTAL PART

2.1 Equipment

2.1.1 Thermal Analysis (TA)

Thermograms were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) modes. They were carried out on a Netzsch instruments. The models used were DSC 200 cell and TGA 209 cell, respectively, with TASC 414/3 controller. Hermetically sealed aluminium pans were used for DSC studies, while platinum pans were used for TGA. Sample sizes were about 10-20 mg, and the experiments were carried out in N₂. For DSC measurements, a N₂ purge flow rate was set at 40 mL/min, and for TGA measurements, it was set at either 60 or 40 mL/min. The temperature analysis range in the DSC was from 25° to 450°C, at a heating rate of 10°C/min, while TGA measurements were conducted from 25° to 900°C, with a heating ramp rate of 20°C/min.

2.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were acquired using a FT-45A Bio-Rad instrument. KBr was pressed hydraulically into pellet and rapidly taken to the FT-IR sample chamber. The chamber was purged with N₂ for 20 min to remove CO₂ before initiating data acquisition. The KBr spectrum background was collected with a minimum of 64 scans. After the background spectra, the sample was

then mixed with dried KBr at an approximate ratio of 1:20 sample:KBr. The resolution for this method was $\pm 4 \text{ cm}^{-1}$.

2.1.3 Nuclear Magnetic Spectroscopy (NMR)

^1H - and ^{13}C -NMR spectra were obtained on a 500 MHz JEOL spectrometer at room temperature at the Scientific and Instrumental Research Equipment Center, Chulalongkorn University. Deuterated dimethyl sulfoxide (DMSO- d_6) was used as solvent. ^1H -NMR spectra were recorded at 10,000 Hz using 16 scans, a pulse width and a pulse delay of 5.5 sec and 30 sec, respectively and a sweep width of 16,000 Hz. ^{13}C -NMR spectra were recorded at 9065 Hz using 4,000 scans, a pulse width of 4.75 sec, a pulse delay of 2.5 sec and a sweep width of 20,000 Hz. Tetramethylsilane (TMS) was used as the internal reference.

2.1.4 Melt Rheometer

The storage modulus and loss modulus of polymer film were examined using a melt rheometer by Rheometric Scientific Instrument model RES. The measurement was carried out using dynamic strain sweep mode and dynamic temperature ramp mode. Dynamic strain sweep mode was used for measuring the appropriate strain that gave the constant shear modulus. This strain was then used in dynamic temperature ramp mode to measure the storage modulus and loss modulus by variation of temperature from 25-250°C with the temperature ramp of 5°C/min.

2.2 Materials and Method

All glasswares used for these experiments were dried in an oven at 110°C. Starting reagents and solvents were dried prior to use, and reactions were carried out in an inert atmosphere (nitrogen).

Fused silicon dioxide or HI-SIL 927 silica (SiO_2), with a surface area of 182 m^2/g , by BET, was donated by PPG Siam Silica Co., Ltd. It was used as received. Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, EG) and Glycerol [$\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$] were purchased from Farmitalia Caro Erba (Barcelona). EG was distilled in a fractional distillation set and used as both reactant and solvent. Glycerol was used as received. Triethylenetetramine ($\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_3\text{H}$, TETA), donated by Union Carbide Thailand Limited, was used as a base after under pressure distillation prior to use. Acetonitrile (CH_3CN) and methanol (CH_3OH , MeOH), purchased from J.T. Baker Inc. (Philipsburg, USA) and purified by distillation over calcium hydride and magnesium activated with iodine, were used as precipitating agents, respectively. Dioctyl phthalate (DOP), purchased from Fluka, was used as received, as a plasticizer.

2.3 Procedure

2.3.1 Synthesis of Glycolato Siloxane Polymer

Effect of TETA Concentration on Glycolato Siloxane Products

Synthesis of glycolato siloxane polymer was carried out by placing 15.00 g (250 mmol) of SiO_2 , 3.66 g (25 mmol, 100 mmol of N equivalents) of TETA and 150 mL of ethylene glycol (EG) into a 500 mL, three-necked reaction flask. The reaction took place in a simple distillation set up under N_2

atmosphere. The reaction mixture was magnetically stirred and heated to distill off ethylene glycol and by-product, water, produced during the reaction. During the course of reaction, an equal amount of fresh and dry EG to amount of EG distilled off was added and distillation was continued until the reaction mixture was clear.

This procedure was repeated with other TETA concentrations of 5.40 g (37.5 mmol, 150 mmol of N equivalent), 7.31 g (50 mmol, 200 mmol of N equivalent), 9.14 g (62.5 mmol, 250 mmol of N equivalent) and 10.97 g (75 mmol, 300 mmol of N equivalent). The reaction mixtures were allowed to heat for 25 h, till the mixtures were clear solution, meaning that the reaction was finished.

2.3.2 Crosslinking Step with Glycerol

Addition of Glycerol after the Synthesis of Glycolato Siloxane

Glycolato siloxane polymer product was first synthesized by using 15.00 g (250 mmol) of SiO₂, 3.66 g (25.00 mmol) of TETA, and 150 mL of EG. Reactions were run at the boiling point of EG (~200°C). During the course of reaction, an amount of fresh EG was added to replace the amount of EG coming off the system. After 25 h, a stoichiometric equivalent of glycerol, 23.00 g (250.00 mmol) to SiO₂ was then added. The mixture was further heated at 100°C under high vacuum (10⁻² Torr) for 20 h. The obtained mixture was cast as films in a vacuum oven at 80°C. This procedure was repeated with other TETA concentrations 5.40 g (37.5 mmol, 150 mmol of N equivalent), 7.31 g (50 mmol, 200 mmol of N equivalent), 9.14 g (62.5 mmol, 250 mmol of N equivalent), and 10.97 g (75 mmol, 300 mmol of N equivalent).

2.3.3 Effect of Crosslinking Reaction Time on the Crosslinked Polymer Products

Glycolato siloxane polymer was obtained from using 15.00 g (250 mmol) of SiO₂, 3.66 g (25.00 mmol) of TETA and 150 mL of EG. This reaction was run at the boiling point of EG for 25 h under N₂. 23.00 g (250 mmol) of glycerol and 0.49 g (0.5 mol%) of dioctyl phthalate were then added into the product mixture, followed by heating at 100°C under high vacuum (10⁻² Torr). A sample was collected at 10, 15 and 20 h, respectively, and divided into 2 portions. One portion was cast as a film in a vacuum oven at 80°C. The other was precipitated in 2.5% of dried MeOH in dried CH₃CN.

This procedure was repeated with different TETA concentrations of 5.40 g (37.5 mmol, 150 mmol of N equivalent), 7.31 g (50 mmol, 200 mmol of N equivalent), 9.14 g (62.5 mmol, 250 mmol of N equivalent), and 10.97 g (75 mmol, 300 mmol of N equivalent).

2.3.4 Effect of Dioctyl Phthalate Concentration on Crosslinked Products

Crosslinking polymer was obtained via the procedure in 2.3.2, except that dioctyl phthalate of 0.2 mol% (0.20 g) was also added simultaneously with glycerol. The obtained mixture was divided into 2 portions. One portion (~50 mL) was cast as films in a vacuum oven at 80°C. The other (~50 mL) was precipitated in 2.5% of dried MeOH in dried CH₃CN.

The same procedure was again repeated with 0.29 g (0.3 mol%), 0.39 g (0.4 mol%), and 0.49 g (0.5 mol%) of dioctyl phthalate.