CHAPTER III

EXPERIMENTAL

3.1 Materials and equipment

3.1.1 Chemicals:

Fumed silica (SiO_2)
Triethanolamine (TEA)
Ethylene glycol (EG)
Acetonitrile
Hydrochloric acid (HCl)
Potassium hydroxide (KOH)
Isopropanol (IPA)
3-Aminopropyltriethoxysilane (3-APS)
3-Glycidoxypropyl-trimethoxysilane (GPTS)
Silicone oil
PMMA substrates

3.1.2 Equipment:

Thermogravimetric Analyzer (TGA), (DuPont TGA2950)
Fourier Transform Infrared Spectrometer (FTIR), (Bruker instrument, model EQUINOX55)
Positive Fast Atomic Bombardment Mass Spectrometer (FAB^+-MS), (707 VG Auto spec-ultima mass spectrometer, Manchester, England)

3.2 Experimental procedures

3.2.1 Silatrane synthesis

Following the method of Wongkasemjit [11], silatrane were synthesized directly from inexpensive and widely available starting materials via the Oxide One Pot Synthesis (OOPS) process, which is the one step reaction.

Silatrane (SiTEA) was synthesized by heating a mixture of 0.125 mol of triethanolamine, 0.1 mol of SiO_2 and 100 ml of ethylene glycol at 200°C under nitrogen atmosphere. The reaction was complete within 10 h and the mixture was cooled down to room temperature. Then the excess ethylene glycol was distilled under vacuum (8 mmHg) at 110°C for 6 h. The white solid was washed three times with dried acetonitrile to remove the unreacted triethanolamine and ethylene glycol. The silatrane product was dried under vacuum desiccator overnight and characterized using TGA, FAB^+-MS and FT-IR.

3.2.2 Suspension and coating preparation

Before obtaining a successful preparation of hard-coating solutions for PMMA, there were a number of fail experiments, which are worth nothing. In the first fail trial, solutions of silatrane and polyvinyl alcohol (PVA) were prepared by mixing 1 g of silatrane with 10 ml of solutions of PVA in water with the concentration ranging from 4 to 6 w/v % (based on weight of PVA per volume of water). Potassium hydroxide (KOH)-etched PMMA was then dip-coated in these solutions, pre-cured at 60°C for 30 minutes, and then cured at 120°C for 2 hours. Even though the coating layer was transparent, it was soluble in water. In the second fail trial, partially hydrolyze silatrane solution was prepared by dissolving an amount of silatrane in isopropanol (IPA), using 1 M HCl as the catalyst. Various amount of 3-methacryloxypropyltrimethoxysilane (MPTS) was then added to the silatrane solution and stirred for 24 hours. The weight to weight ratio between MPTS and silatrane was varied between 0 and 10 (i.e. 1, 3, 5, 7 and 10 respectively). KOH-etched PMMA was then dip-coated in these solutions, pre-cured at 60°C for 30 minutes, and then cured at 120°C for 2 hours. The resulting coating layer appeared to be yellow in color and the pre-curing solutions prepared tended to phased-separate rather easily. In the third fail attempt, glycidoxypropyltrimethoxysilane (GPTS) was used to prepare the pre-curing solutions of silatrane instead of MPTS. Before dip-coating PMMA in the solutions, diethylenetriamine (DETA) in various amounts ranging from 1 to 5 wt % (based on weight of DETA per total weight of the pre-cured solutions) was added to the pre-curing solutions. Coated PMMA substrates were pre-cured at 60°C for 30 minutes, and then cured at 120°C for 2 hours. The coating layer was improperly cured. In the forth successful attempt, aminopropyltriethoxysilane (APS) was used as the curing agent instead of DETA. It was found that among the various amounts of APS of APS added (i.e. from 1 to 5 wt.%), 3 wt.% was the best in giving the resulting curing or hard-coating solutions in the conditions appropriate for dip-coating for a long enough time (i.e. long enough gelation period). The resulting coating layer was found to be transparent, but the adhesion between the coating layer and the PMMA substrates were not good as the coating layer could be peeled off from the substrate surface rather easily. In order to improve the interfacial adhesion between the coating layer and the PMMA surface, plasma etching was utilized along with chemical etching in a KOH solution.

Silatrane powder was dissolved in 1M HCl then isopropanol (IPA) was added in the mixture. The pH was measured immediately after the addition of the IPA. 3-Glycidoxypropyltrimethoxysilane (GPTS) was added to the silatrane solution during vigorous stirring and stirred for 24 h. The solutions were prepared at various GPTS/silatrane weight ratio (R = 1, 3, 5, 7 and 10). The coating solutions were characterized by FTIR. The various composition of coating solution is presented in the table 3.1

Table 3.1 The various composition of coating solution.

Composition	silatrane (g)	GPTS (g)	GPTS / silatrane	APS (μl)		
				3%	**4%**	**5%**
R0	0	0.5	0	69	92	115
R1	0.1	0.1	1	57	76	95
R3	0.1	0.3	3	63	84	105
R5	0.1	0.5	5	69	92	115
R7	0.1	0.7	7	75	100	125
R10	0.1	1	10	84	112	140

1M HCl : IPA = 600 : 1200 μl

The example of this procedure, the following steps were used to prepare a suspension with GPTS/silatrane ratio of 1. Silatrane powder (0.1 g), 1M HCl (600 μl) and IPA (1200 μl) were mixed in vial. GPTS (0.1 g) was then added to the suspension with vigorous stirring for 24 h.

Coating was prepared by dipping-withdrawing manner of the PMMA sheet (1.5 x 7 x 0.3 cm^3) in the coating solution at the room temperature. To improve the adhesion between substrates and the coating solution, the PMMA sheet was treated with plasma and chemically by using 10-wt% aqueous potassium hydroxide solution for 5-10 minutes at the temperature of 20°-60°C in the ultrasonic bath. These substrates were washed by de-ionized water twice and dried in oven to evaporate residual water. Before dipping, 3-Aminopropyltriethoxysilane (3-APS) was added to the GPTS/silatrane suspension. The APS was used to cure the epoxy groups. The amount of APS was kept constant for all suspensions at 3-wt% of total weight. Coating was made within 0.5 h after APS addition. The wet coating PMMA was placed in a drying oven with air convection for 0.5 h at 60°C, followed by 2 h at 120°C. These heating conditions were chosen to achieve both the drying (60°C) and curing (120°C).

3.3 Analytical Procedures

3.3.1 Thermogravimatric analysis (TGA)

Thermogravimatric analysis was carried out on a DuPont instrument, DuPont TGA2950. Approximately 5-10 mg of sample was placed on a platinum pan and heated under nitrogen atmosphere at a flow rate of 25°C/min. The temperature program was started from room temperature to 750°C, with a heating rate of 10°C/min.

3.3.2 Fourier transform infrared spectroscopy (FTIR)

Chemical characteristics of precursors and organometallic coating component was analyzed using FTIR spectroscopy, Bruker instrument, model EQUINOX55. The precursor sample (0.6-1.2 μm thickness) was ground and pressed to form a pellet with dried KBr and the sample solution were coated on the ZnSe crystal.

3.3.3 Positive fast atomic bombardment mass spectroscopy (FAB^+-MS)

The precursor sample was characterized using FISONS Instrument (707 VG Auto spec-ultima mass spectrometer, Manchester, England) with a VG data system, employing a direct probe inlet and using the Cs gun to ionize sample mixed with glycerol matrix. The mass range of sample was set from $m/z = 20$ to 1500.

3.4 Testing Procedures

3.4.1 Adhesion property test by "direct method" [23]

The direct method is used to provide a quantitative index of the thermal cured coating on the substrate. The technique is based on the first forming and adhesive bonding with the coating material. Force is applied to determine a value for practical adhesion. The force required to pull the film off the substrate is F. The stress of adhesion is σ. The unit area is A where A was 0.5 cm^2 in this study.

$$\sigma \quad = \quad F/A \tag{3.1}$$

3.4.2 Scratch resistance test by steel wool abrasion [24]

This test is performed using #000 grade steel wool. The steel wool is rubbed across the PMMA surface with 1.0 kg (2.2 lbs) force continuously applied for 10 cycles. This rubbing can be done using an oscillating machine or by hand. The surfaces are graded as "pass" if the scratching is less than 40. Observation result of coated PMMA is compared with uncoated one and the degree of scratch surface is measured by using optical microscope.