CHAPTER II

EXPERIMENTAL

A sheet molding compound is made by mixing resin and other ingredients to form a homogeneous paste. In this system, glass fiber, resin, filler and other ingredients are combined into a sheet form that can easily be laid down in a mold. The mixing action requires that the viscosity of the compound be low not more than 3×10^4 mPa-s but in actual practice the compound must reach a high viscosity in several million mPa-s to attain a tack-free, handleable form. The prime factor initially encountered in sheet preparation and impregnation is a suitable formulation, in order to get homogeneity resin mix. A small amount of magnesium oxide was added as thickener in formulation, so as to increase the viscosity of the system very rapidly. Although MgO usually dissolves somewhat in styrene monomer, its solubility still depending on the extent of concentration. The best mixing process should be realized in the step of formulation, the particle size of MgO, $CaCO_3$ and the speed of rotatng stirrer are the influencial parameters.

The preparation of the sheet compound is an important step in SMC process. If the sheet compound is not properly prepared, entrapped air bubble can result in a pit or porosity which is the major surface defect (Figure 5 in APPENDIX G).

This porosity results in excessive repairing of the SMC parts and must be rejected accordingly. When the SMC sheet is ready to be molded in a compression mold, the duration of cure is another factor in molding. One of the techniques of molding is that the chemical reaction is usually fast, therefore rapid closing and opening of mold are required. The actual molding cycle involves simply loading the mold, closing the press, degassing and thus completing the cure. However, there are more elaborate techniques which are required, such as a slow close or a dwell period, to give the best molded parts. Most exhausted times are used in trial and error to SMC procedure. There are many of molded materials or parts unacceptable and repeatability of the procedure is unavoidable. The methods are briefly described in the following section.

2.1 Instruments and Equipment

Compression Molding : A 6 kN laboratory sized hydraulic press.

Oven : An Isotemp Oven, 200 series, model 230^{o}F, FISHER COMPANY.

Mechanical stirrer : KIKA Lab., RN 28W, Janke & Kunkel.

Viscometer : Digital Brookfield Viscometer, model RVT-D.

Durometer : Shore Durometer, Type A, The shore Instrument & MFG. Co., New York.

Contour Cut Specimen : Ceast - Contour Cut, code 6490, serial 8412, Torino/Italy .

Universal Testing Machine : Instron UTM, model 4206.

Impact Tester (notched Izod Type) : Capacity 10 ft.lb, AVERY type 6702, England.

Scanning Electron Microscope : Model JSM-T20, JEOL Co., Japan.

2.2 Chemicals & Materials

Materials and sources of supply used in SMC compounding are shown in Table 2.1. The unsaturated polyester resin used in this study was a general commercial grade, Alpolit UP 355E, from Hoechst Thai Co.Ltd., which contains 33% of the styrene monomer in solution. Some physical characteristics of the resin are illustrated in Table 2.2. The catalyst in the system is t-butyl perbenzoate. The filler is $CaCO_3$ from Silathip Saraburi Co., Ltd. It is a special grade of coated fine particles of calcium carbonate powder which has the average particle size about 2 micrometers. The surface of this calcium carbonate was treated with stearic acid which is compatible with the organic medium such as polyester resins. Some properties of calcium carbonate (trade-name, Sila Flex 3 CG) are shown in Table 2.3. In addition, there is untreated $CaCO_3$ or purified $CaCO_3$ (trade name, Microkal KP, Silathip Co. Ltd.) which is also used in the experiment to study the effect of different types of fillers on viscosity.

Table 2.1 Materials and sourcesof supply used in SMC compounding

Materials	Chemical name	Trade name	Source of Supply
Resin	unsaturated polyester resin	Alpolit UP 355E	Hoechst Thai LTD.
Catalyst	t-butyl perbenzoate $C_6H_5\overset{O}{\overset{\|}{C}}OOC(CH_3)_3$	TBP	Sanken Chemicals Co.
Filler	calcium carbonate, $CaCO_3$	Sila Flex 3 CG	Silathip Saraburi Co., Ltd.
Thickener	magnesium oxide MgO	magnesium Oxide	Rieldel-De Haenag, Hannover
Mold Release	zinc stearate, $(Zn(C_{18}H_{35}O_2)_2$	zinc stearate Emulsion	Gentra International Co.Ltd. -
Reinforcing Material	glass fiber, (Chopped Strand mat)	Mat 700	ACI Fibreglass Co.

Table 2.2 Some physical properties in specification of resin UP-355E (14)

Property	Value	Test Method
Specification of the resin as received:		
Viscosity at 20°C, mPa-s	1100-1300	DIN 51550
Content of styrene, %	33±1	-
Density at 20°C, g/cm^3	1.13	DIN 51757
Storage stability at 25°C in darkness, months	at least 6	-
Specification of the cured resin :		
Tensile strength, MPa	54	DIN 53455
Elongation, %	2.0	DIN 53455
Flexural strength, MPa	108	DIN 53452
E-modulus, MPa	3,138	DIN 53455
Impact strength with notch, J/m	10.0	DIN 53453

Table 2.3 Some physical properties of treated $CaCO_3$, Sila Flex 3 CG special grade (15).

Property	Value
Average particle size, micrometer	2.0
Oil absorption (DOP), g/100g	21.00
Moisture content, %	0.15
Specific gravity	2.70
Colour	white
Stearic acid, % treated on the surface	1.0

The thickener used in the system was magnesium oxide (light powder product type). The reinforcing material is chopped strand mat of glass fiber. The individual glass strands are approximately 50 mm long and randomly distributed to give minimum orientation of glass fibers. It is a medium bulk mat with 450 g/m^2, specifically designed as a general purpose mat. The chemical coating, or size, which is applied to each filament of glass and which contains a silane coupling agent to effect a superior bond between the glass and resin, is compatible with polyester resin. The glass strands are bound by a poly (vinyl acetate) emulsion binder which gives the mat excellent strength and flexibility for easy handling of the roll.

2.3 Formulation for SMC

One type of formulation for SMC is shown in Table 2.4 . By varying the amounts of filler from 0% to 80% by weight of the resin and the amounts of glass fiber from 20-40% by weight of the resin mix or paste compounding, the amounts of catalyst, zinc stearate and magnesium oxide are controlled for all formulations .

Table 2.4 One type of formulation for SMC

Ingredients	Resin Mix	Ratio of Sheet Formation	% Final Composition
1. Resin, UP 355E (inclusive of styrene)	100		48
2. Catalyst, t-butyl perbenzoate	1		0.5
3. Thickener, magnesium oxide	2-4	70	1.5
4. Filler, calcium carbonate	40		19
5. Internal mold release, zinc stearate	2		1
6. Reinforcing material, glass fiber	-	30	30

2.4 Mixing Procedure for SMC

The steps in the mixing procedure for the preparation of one SMC compounding were begun with a batch-mixing process. The liquid catalyst was to be preblended with styrenated resin (UP 355E) prior to batch addition. Divided the catalysed resin in two parts, the first was for filler mix and the second for thickener solution.

2.4.1 Mixing Method

1. Added the resin (UP 355E) in a cylindrical glass mixer and start mixing, stirred for 3 to 5 minutes.
2. Added the catalyst and stirred for about 30 minutes until all were well dispersed.
3. Added the preblended catalyst-resin mix and stirred for 5 to 10 minutes until all were well dispersed.
4. Added the filler and mix for about 30 minutes until all were well dispersed.
5. Added the thickener solution (prior preparation of MgO and resin) in the main glass mixer and stirred for 5-10 minutes.
6. Stopped the mixing and cleaned the stirrer rod with acetone. Resin mix may start to thicken immediately, as shown in the section 2.4.2.

2.4.2 Control of the Viscosities

The instrument for measuring the high viscosity of the resin mix for SMC is a Brookfield RVTD viscometer mounted on a Brookfield Helipath Stand:

1. The original resin viscosity with styrene monomer : 800-900 mPa-s.
2. After the catalyst addition: about 700-800 mPa-s.
3. After the filler addition: about 2,000-15,000 mPa-s.
4. After the thickener addition: about 3,000-30,000 mPa-s.

2.5 SMC Sheet Preparation

1. Weighed the resin mix that previously contained the particulate mineral filler together with the catalyst and thickening agent, as the required composition.

2. Poured the resin mix on a layer of polyethylene film (PE film) and then layed with 6x6 inches in size of chopped strand glass fiber mat.

3. Covered with another PE film and then kneaded to eliminate entrapped air with the roller. The glass fiber could impregnate or wet out with the resin mix into a sheet form just similar to a sandwich between two layers of PE film.

4. For the preparation of SMC sheet, the glass fibers became consolidated with the filled resin, forming a homogeneous sheet, which was then brought to the hot oven for maturation.

5. Allowed the resin to thicken to a moldable consistency. Brought the SMC sheet into the oven at the temperature 36°C, so as to age SMC sheet from 24 to 36 or 72 hours before molding in order to obtain an optimum thickening.

2.6 Molding Procedure

2.6.1 Start up the Molding Machine

1. Cleaned the mold surface by a soft brush and rubbing off adhered resin spots with wollen material. The flash from, the previously molded part and the shear edge must be completely cleaned off, all chips must be removed from the mold surface.

2. Treated the external surface of the mold by waxing with mold release (TR-104, Hi-temp grade) for the release of the SMC finished product.

3. Set the mold temperature at 140-150°C and the pressure at 3.5-7.5 MPa.

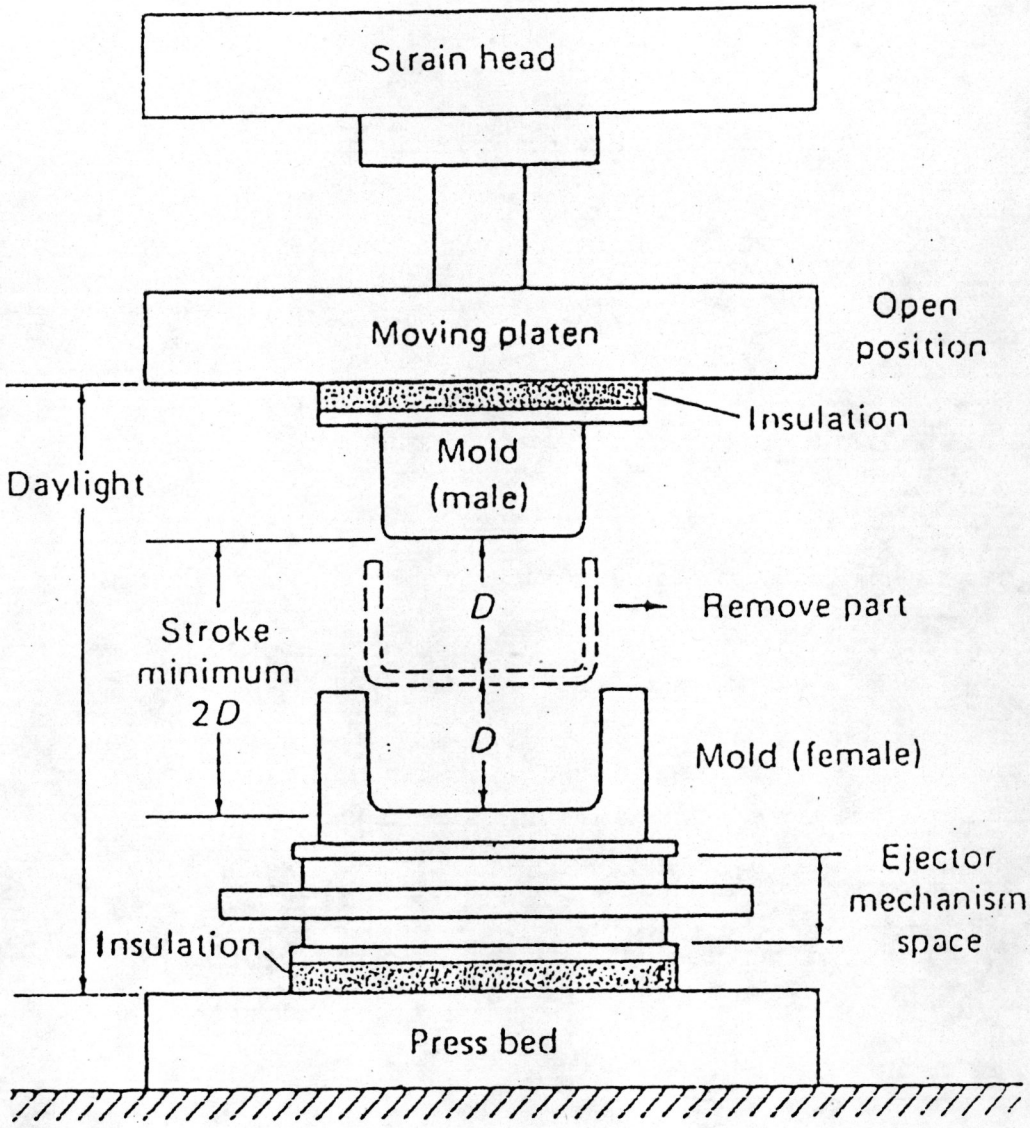

Figure 2.1 The compression mold.

2.6.2 Preparation of SMC Charge

1. Weighed SMC charge and cut into a rectangular shape of 6x6 inches which covered up to 80-90% of the mold area.

2. Removed the PE film from both sides of the sheet. Placed the SMC charge in the mold.

3. Closed the mold. The curing time was set at 2-4 minutes, after that the mold was opened.

4. Removed the molded parts from the mold. The compression mold is shown in Figure 2.1.

Typical Cycle Time :

Loaded SMC Sheet	6	sec
Closed mold	7	sec
Cure	120	sec
Opened mold	7	sec
Part removal	60	sec
Total	200	sec

2.7 Methodology of Determining the Effect of $CaCO_3$ and MgO on viscosity

2.7.1 The Effect of Filler on Viscosity

Two kinds of $CaCO_3$ filler were used to determine the effect on viscosity. One was the treated $CaCO_3$, Silaflex 3CG,

with stearic acid, $CH_3(CH_2)_{16}COOH$ and the other was the untreated $CaCO_3$, Microcal KP. Both $CaCO_3$ are commercial grades which have the same particle size and other similar compositions.

1. Mixed the polyester resin and the calcium carbonate filler at the composition of 40% by weight of resin. Both treated and untreated $CaCO_3$ were used.

2. Poured the $CaCO_3$ filled resin into two cylindrical glass-containers.

3. Measured the viscosity of both mixtures by a Brookfield RVTD viscometer.

4. Sealed both mixtures in glass containers with aluminium foil.

5. Stored at 2 different conditions, one at 36°C and the other at room temperature, 28°C.

6. Measured their viscosities at different time periods.

7. Repeated the same procedure on steps number 1-5 with the compositions of 80% and 120% $CaCO_3$ by weight of the resin.

8. Determined the effect of $CaCO_3$ on viscosity by plotting viscosity profile between the viscosity and the amounts of $CaCO_3$.

2.7.2 The Effect of Thickener on Viscosity

Magnesium oxide was used as thickener in this system. A test to determine the thickening rate of MgO thickened into the $CaCO_3$ filled polyester paste was carried out. Viscosity was determined at different time periods for the development of a thickening profile. The following steps were carried out.

1. Mixed the polyester resin and MgO at three different compositions : 3%, 5% and 7% MgO by weight of the resin in the form of paste.
2. Poured each of the thickened polyester resin into two containers.
3. Measured the viscosity of each composition by a Brookfield RVTD viscometer.
4. Sealed with aluminium foil.
5. Stored at two different conditions, one at 36°C and the other at room temperature (28°C).
6. Determined the effect of MgO on viscosity by plotting viscosity profile between the viscosity and the amounts of MgO.

2.7.3 The Effect of Filler and Thickener on Viscosity

1. Mixed the polyester resin, $CaCO_3$ and MgO at different compositions which were listed in Table 2.5.

Table 2.5 A list of formulations in the programmed testing of viscosity profile

% $CaCO_3$ in Resin	The amounts of MgO in Resin (%)			
	0%	3%	5%	7%
0	/	/	/	/
40	/	/	-	-
80	/	/	-	-
120	/	/	-	-

Note / denotes for the composion tesing

2. Poured the thickened mixture into a glass container, determined the viscosity, sealed with aluminium foil and then let for aging under control condition. The experiment was then carried out by following the steps in the section 2.7.2.

Each glass container of different compositions was sealed and stored at two constant temperatures, the room temperature (28°C) and 36°C.

2.7.4 Determination of the Viscosity Profile

1. Determined the viscosity by a digital Brookfield RVTD viscometer. This reading was known as the "0" point of the thickening time.

2. Determined the viscosity of mixture at the end of the first 2 hours after the "0" point.

3. Determined the viscosity of the mixture at the end of the programmed times; 10, 20, 30, 40, 50, ... hours until the final thickening that was measurable. Maximum measurable viscosity by Brookfield RVTD viscometer is 8 million mPa-s.

4. Measured data was plotted as the disired degree of thickening for molding and a quality control function.

2.8 Determination of the Storage Life

1. Prepared the SMC paste by mixing with 3% MgO, 1% t-butyl perbenzoate, 2% zinc stearate, all the compositions were based on the weight of resin.
2. Added all these compositions with the resin and glass fiber in different ratios as indicated in Table 2.6.
3. Covered with polyethylene films for SMC sheet. The steps of mixing and SMC sheet preparation are shown in sections 2.4 and 2.5

Table 2.6 Typical formulation of SMC sheet for the determination of its storage life

Compositions	MgO	t-butyl perbenzoate	Zinc Stearate
*R 30, F 0	3%	1%	2%
R 40, F 0			
R 30, F 40			
R 25, F 60			
R 30, F 60			
R 40, F 60			

Note * R 30 : 30% by weight of glass fiber in the resin mix, F0 : 0% or no $CaCO_3$ in the resin

4. Allowed maturation in an oven at the temperature of 36°C for 2-3 days.
5. Cut the SMC sheet as the specimen into a size of 3x3 inches.
6. Measured the hardness of the SMC sheet in a unit of shore scale by a Shore Durometer (type A). Testings were taken for 5 points : 4 points at the corners and 1 point at the center of each SMC specimen.

7. Repeated the hardness testing every week (7 days), until the specimen became too hard or tough to press with a needle incorporated in Shore Durometer.

2.9 Preparation of Sample for SEM

1. Selected the sample which had been tested for the tensile, flexural and impact properties for this studying.
2. Cut these samples cross-sectionally into small pieces for scanning electron microscopy (SEM).
3. Coated the surface of each sample (with gold by Ion Sputtering method by using Edward Sputter Coating Device, model SCD-040, Balzers Union) at an excitation voltage of 15 KV.
4. Scanned and photographed the samples by SEM, model JSM-T20, Jeol Co.

2.10 Characterization of the cured SMC: Mechanical Properties

(Methods of testing, preparations of specimen and calculations were described in APPENDIX C).

2.10.1 Tensile Properties

Standard Test	:	ASTM D638M-86.
Equipment	:	Instron UTM, model 4206 (5 tons in capacity).
Shape	:	dumbell (type M-1).
Dimension	:	10 mm width of narrow section, 50 mm of gauge length and 150 mm of length for overall.
Number of test	:	at least 3 specimens of each sample.
Assessment	:	tensile strength at break, and tensile modulus.

2.10.2 Flexural Properties

Standard Test	:	ASTM D790M-86.
Equipment	:	Instron UTM, model 4206 (5 tons in capacity).
Shape	:	rectangular.
Dimension	:	10 mm in width and 100 mm in length.
Number of test	:	at least 3 specimens of each sample.
Assessment	:	flexural strength at break, and flexural modulus.

2.10.1.3 Impact Resistance

Standard Test	:	ASTM D256M-86.
Equipment	:	Impact Tester (Izod), AVERY type 6702, 10 ft-lb in capacity.
Shape	:	rectangular (notched).
Dimension	:	see APPENDIX C.
Number of test	:	at least 3 specimens for each sample
Assessment	:	energy to break or Izod Impact Strength, J/m.