

## CHAPTER I

### INTRODUCTION

Reinforced plastics, a relatively new family of engineering materials, have grown rapidly in recent years. They consist of polymer matrices, reinforcements and other materials such as fillers. By far the most widely used polymer matrices are unsaturated polyester resins and the reinforcements are glass fibers.

Glass fiber reinforced polyester composites have received an increasing attention from the automotive industry. Such composites offer combinations of properties which are not found in other materials. High strength, dimensional stability, low weight, corrosion and chemical resistance are some of the properties searched by the designers.

Polyester compounds suitable for hot press molding process, known as sheet molding compounds (SMC), bulk molding compounds (BMC) and thick molding compounds (TMC), have been developed in industry, providing processors (e.g., the automotive industry) with formulating and processing flexibility and the inherent strength needed to meet the requirements of specific applications (1). Depending upon the application and the manufacturing process selected, a number of other additives are employed to provide specific products or end use properties.

### 1.1 Definition and History of SMC

Sheet Molding Compound (SMC) refers to both a material and a process for producing glass fiber reinforced polyester resin items (2). SMCs as known in the plastics industry, are composites ready for fabrication that have been molded by combining a thermosetting resin matrix with reinforcing fiber and other modifiers in a form of sheet. In a sheet form, SMC can easily be laid into the mold, either manually or by automatic mechanical handling techniques. More detail of each process is described later. Originally, SMC was called prepreg, which was referred to thin or single-ply nonwoven reinforced fiber sheets, usually impregnated with a thermoset resin. The term prepreg caused confusion, however, the Society of the Plastics Industry has designated the material as sheet molding compound (3).

The term SMC was adopted by the Society of the Plastics Industry to denote a resin impregnated chopped-strand glass fiber in dry sheet form. SMC was first prepared in the fiber glass reinforced plastics (FRP) by the Farbenfabriken Bayer Co. in the early 1960s. Its use spread quickly through Europe and Japan, mostly in the electrical and communications industries. In 1965, the U.S. Rubber Co. introduced an SMC under the trade name Vibrin Mat. In 1966, the General Tire and Rubber Co. introduced Structoform. In the following years, Owens-Corning Fiberglas Corp. developed SMC systems which used glass roving and low shrinkage polyester resin. This development of so-called low



profile SMC marked the beginning of high volume automotive applications (3). Since the early 1970, the Chevrolet Corvette body has been fabricated with SMC. In 1983, another all-plastic-body car, Pontiac Fiero, was introduced. All horizontal panels, including the hood, roof, deck lid, and rear upper quarter panels are made of SMC as shown in Figure 1.1, nearly 40 kg are used for these parts (4).

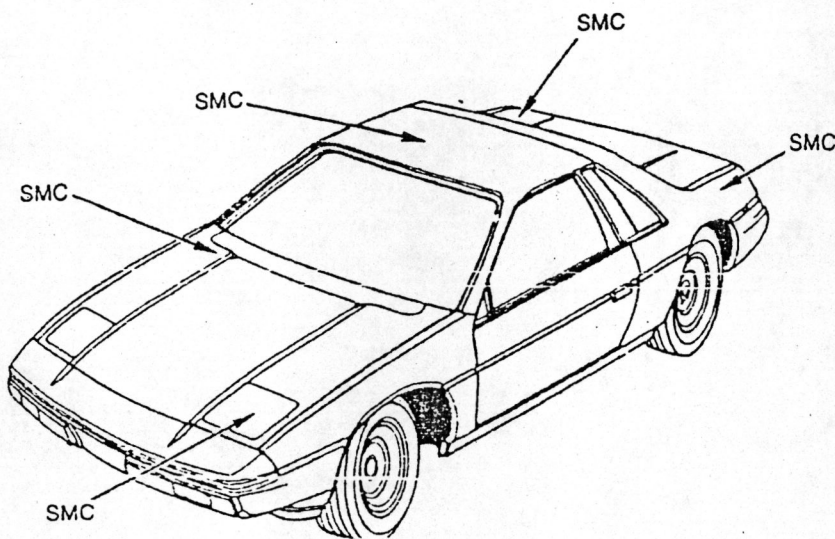


Figure 1.1 The SMC parts of Pontiac Fiero

## 1.2 Materials and Their Functions

### 1.2.1 Resin : Unsaturated Polyester

Resins used with fibrous reinforcements to produce plastics serve a number of purposes (5). Although the reinforcement provides the structural strength, the resin

maintains the desired orientation of the reinforcement, provides for stress transfer from one fiber to another and generates an enclosing armor around each fiber to keep it separated and to prevent abrasion from adjoining fibers. In addition the resin imparts corrosion resistance to the system and contributes to its other properties. Varying the ingredients in the resin system and careful selection of reinforcement make it possible to provide for a wide range of end uses.

Two main classes of resins used for reinforced plastics applications are thermosetting and thermoplastic. The two thermosetting resins primarily used for SMC are unsaturated polyesters and epoxides. Unsaturated polyester accounts for about three-fourths of the resins used in the reinforced plastics industry.

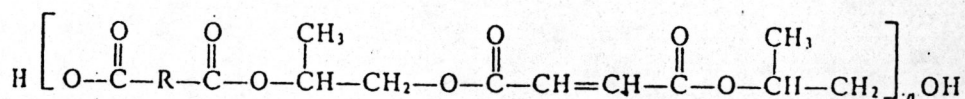
Unsaturated Polyester: The word "polyester" is derived from two chemical processing terms, polymerization and esterification. Technically speaking, polyesters are derived from a production process which involves the condensation esterification of dihydric alcohols and dicarboxylic acids. This reaction covers a wide range of starting materials and can be extended and varied by the substitution or addition of other appropriate starting raw materials. Alteration of the chemical structure by processing techniques and raw material selection is a method of achieving the desired properties in the formulated resins



Because of the versatility of polyesters and their capability to be modified during their chemical construction, they have almost an unlimited range of uses in industry. Polyesters offer the advantage of a balance of good mechanical properties, chemical and electrical properties, dimensional stability, low cost and ease of handling.

Initially one can classify polyester resins into two major types: general purpose resins and special purpose resins. The general purpose polyester is a low cost polyester, with good electrical and mechanical properties and reasonably good corrosion resistance. Special purpose polyesters are those resins which have been specifically formulated to meet some particular end use requirement with respect to performance (5).

The unsaturated polyester resin is generally the reaction product based on a blend of phthalic anhydride and maleic anhydride esterified with propylene glycol (6). The phthalic/maleic mole ratio may range from 2:1 to 1:2. One of the typical polyester resin has the structure shown below, R is the alkyl or aryl group of the modifying dibasic acid or anhydride :



The structure of the backbone of the polyester characterizes the physical properties of the cured resin. In general, as the chain length between the hydroxyl groups increases, flexibility of the cured resin increases. The dibasic aromatic and saturated aliphatic acids are often used in conjunction with maleic anhydride to modify the chemical or mechanical properties of the product. Maleic anhydride provides the unsaturation or reactive site. High unsaturation gives a more reactive resin with improved stiffness at high temperature. Increasing the amount of the saturated component, eg. phthalic anhydride, reduces exothermic curing and stiffness (5).

However, the unsaturated polyester resin can be formulated to suit the requirements of the particular process in which they are going to be used and to emphasize a desired end property. Much of the versatility of unsaturated polyester resin results from the wide selection of raw materials, the basic processing methods and the experience of the manufacture in supplying the resin system that will meet the required product characteristics. Since the formulation of the unsaturated polyester varies with the manufacturer and the intended use.

There are active sites along the chain each of which can be linked to an active site in an adjacent chain using styrene as a link or bridge. The solid is a densely crosslinked rigid solids used with glass fiber reinforcement. Figure 1.2 shows the nature of cured polyester resins; i) structures present



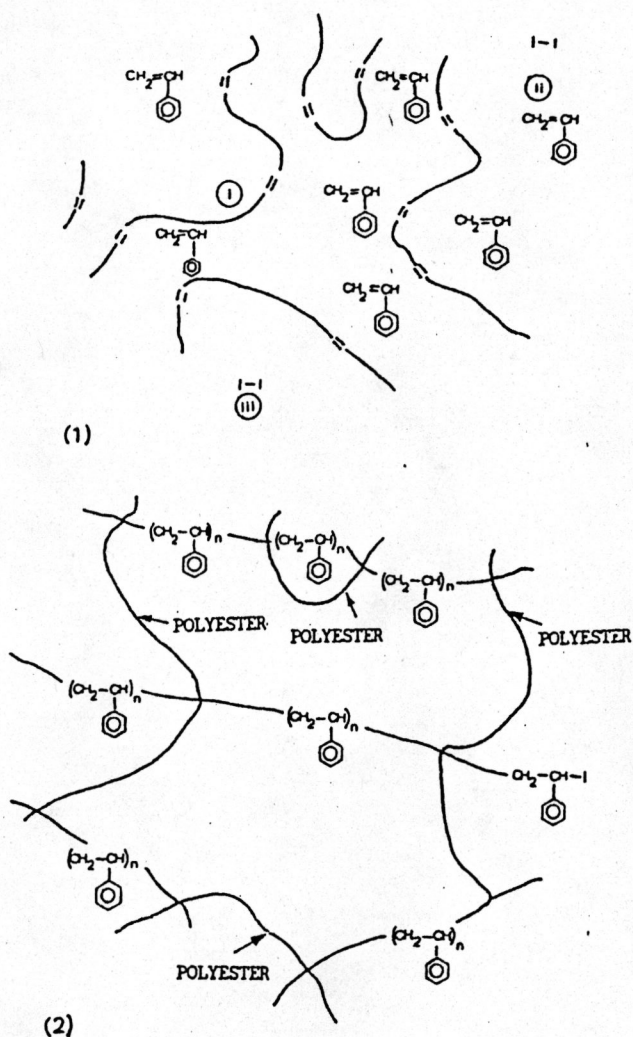


Figure 1.2 The nature of cured polyester resins

(1) Structures present in polyester resin ready for compounding :

- (i) low molecular weight unsaturated polyester molecules
- (ii) reactive diluent (styrene) molecules
- (iii) initiator (catalyst) molecules

(2) Structures present in cured polyester resin.

Crosslinking via an addition copolymerisation reaction. The value of  $n \approx 2-3$  on average in general purpose resins.

in polyester resin ready for molding compound and ii) structures present in cured polyester resin (7).

In working with polyester resin for SMC system, the cure proceeds in two individual stages.

1. The first is the formulation with other compounded materials such as filler and reinforcement in the form of sheet, and then storage at appropriate condition by which the system viscosity increases in a few days.

2. The second phase of the cure takes place rapidly with considerable evolution of heat (exothermic reaction). The crosslinking units as the chains form a three-dimensional network which consequently results in a cured polyester molding compound. In most cases complete cure is obtained without liberation of volatile materials. Completion of curing of the reaction after the addition of the catalyst and heat depends on the formulation. The amount of catalyst, the length of time, and the temperature should be carefully selected for a particular formulation.

#### 1.2.2 Monomer

The resin as normally supplied by the manufacturer contains monomer, but sometimes it may be purchased without monomer. Additional quantities of monomer may be added to the resin at the user's plant (in amounts recommended by the manufacturer) to reduce the viscosity.



Styrene is the most commonly used monomer in unsaturated polyester resin systems because it is abundantly available, low in cost, has good solvent characteristics, and reacts readily with the unsaturated polyester resin during the cure reaction. In summary the main functions of a monomer are (4):

1. To act as a solvent carrier for the unsaturated polyester resin.
2. To modify the viscosity.
3. To enhance selected properties with respect to the end-use application.
4. To provide a completed reaction and cross-linked copolymer.

### 1.2.3 Catalyst

The catalyst initiates the chemical reaction (copolymerization) of the unsaturated polyester and monomer ingredients from a liquid to a solid state. This is the primary purpose of a catalyst. Heat from the mold causes the catalyst to decompose, which activates the monomer and polyester to form cross-linked thermosetting polymers.

Catalysts are only a small part of an SMC resin formulation. Generally, the addition of 0.3 to 1.5 wt% of catalytic agents will adequately promote the cross-linking reaction. Organic peroxides are the principal catalysts used for polyester

SMC. The temperature at which the curing process is to be carried out usually determines the selection of a catalyst (12). There are very wide range of catalyst-accelerator systems for use with resin. The specific requirement of the SMC process, however, limits this choice considerably. The ideal catalyst should allow long ambient-temperature storage life for the sheet, sufficient flow time to adequately fill the mold cavity prior to gelation, and a cure that proceeds as rapidly as possible after gelation to minimize cycle time (6). For any given catalyst-resin system there is an optimum temperature at which the peroxide decomposition initiates the monomer-resin polymerization process. Since SMC is usually molded at temperatures of 132 to 165°C, catalysts that are the most effective as polymerization initiators over this temperature range are the ones used most often. In the experiment, SMC-curing can be catalyzed with a much more stable peroxide catalyst, t-butyl perbenzoate, in order to make a polyester resin molding compound that incorporates calcium carbonate filler together with chopped glass fiber. The peroxyester t-butyl perbenzoate provides adequate storage life, sufficient flow, and satisfactory cure time. It has a 104°C half-life temperature, that will give a lower gel time in the SMC process at elevated molding temperature (6). The t-butyl perbenzoate used in the industry has been proven to give a good result with SMC molding system in that it remains its activity at high temperature and the catalyst cannot polymerize at ambient temperature. From the experiment it can be obvious that the preferred polymerization temperature range is 140-150°C.



The selection of the proper catalyst and the amount to be used for any application depends on the resin type, the curing temperature, the required working or pot life and the gel time. Since none of the available catalysts can meet all of the requirements by itself, combinations of catalysts must be used in order to obtain the best results.

#### 1.2.4 Fillers

Calcium carbonate fillers ( $\text{CaCO}_3$ ) have been proven as the most effective as resin extenders for molding in SMC (7). It can be mixed homogeneously with the resin, with the effect of increasing its viscosity, it therefore becomes more paste-like. The 2 micrometer and 10 to 40 micrometer of particle sizes are the most commonly used. In SMC compound, it is recommended that the 2 micrometer sized calcium carbonate fillers resist settling in resin mix system. In general, fillers are used with polyester resins to help reducing costs. They are much less expensive than the resin itself as well as most of the reinforcing materials. However, there are other advantages associated with the use of fillers. For example, their use permits higher curing temperatures by reducing the concentration of reactive materials. Furthermore, the use of fillers reduces the tendency of the resin to crack during cure, reduces the degree of shrinkage (8) which is illustrated in Figure 1.3.

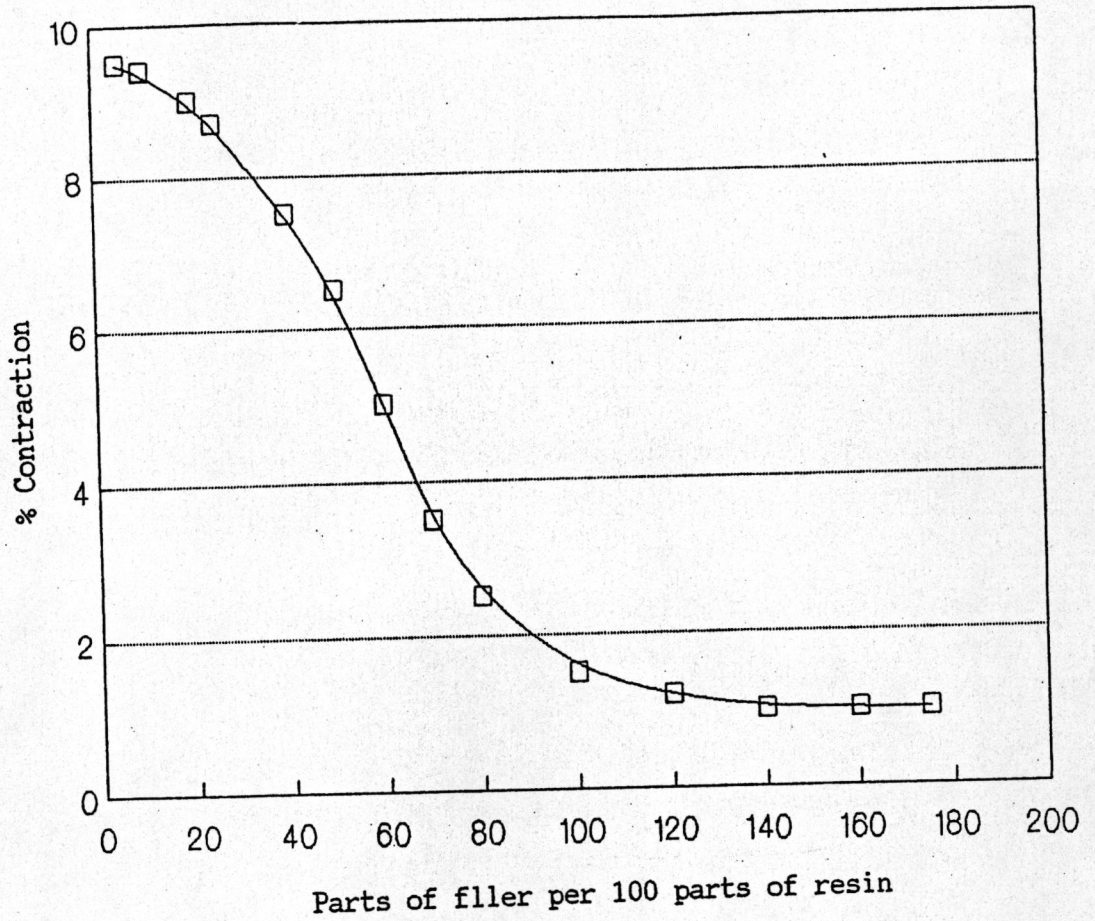


Figure 1.3 Shrinkage related to percent filler added to resin mix.

### 1.2.5 Thickeners

The thickeners include calcium and magnesium oxides and hydroxides. They initiate the reaction that transforms the mixture of SMC ingredients into a handleable, reproducible molding material. Usually 1 to 3% of the thickener are used in the SMC formulation. It is the final ingredient added to the resin mix, and it begins the chemical thickening process immediately (2).



The thickening reaction must:

- i) Be slow enough to allow wet-out and impregnation of the glass reinforcement.
- ii) Be fast enough to allow the handling required by molding operations, as soon as possible after the impregnation step, in order to keep storage inventories low.
- iii) Give a viscosity at molding temperatures that is low enough to permit sufficient flow to fill out the mold at reasonable molding pressures.
- iv) Give a viscosity at molding temperatures that is high enough to carry the glass reinforcement along with the resin paste as it flows into the mold.
- v) Level off in the moldable range to give a long storage life (2).

#### 1.2.6 Release Agents

The release agents are common components of SMC formulations. They are selected on the basis of their melting points being just below that of the molding temperature. In theory, the release agent at the molding compound-mold surface can interfere melts upon contact and forms a barrier against adhesion.

Commonly used internal release agents include zinc stearate, calcium stearate, and stearic acid. Zinc stearate has a melting point of 133°C and can be used at molding temperatures up to 155°C. Calcium stearate, with a higher melting point of 150°C can be used at molding temperatures up to 165°C. Stearic acid should be used only if molding temperatures are below 127°C.

Mold release agents must be used as the lowest concentration possible to do an adequate job, which normally is a concentration less than 2 wt% of the total compound. Excessive amounts can reduce mechanical strength, cause objectionable cosmetic appearance on the molded part surface, and affect paint and/or bond adhesion characteristics (8).

#### 1.2.7 Reinforcements

Many types of reinforcements are used with resin, the glass fibers predominate. Fibrous glass reinforcements are available in many forms: woven fabrics, nonwoven mats, bulk chopped and milled fibers, and unidirectional rovings and yarns.

Rovings are rope-like bundles of continuous untwisted strands for use in such processes as filament winding and pultrusion. They can also be converted into chopped strand mats or cut into short fibers for molding compounds. Chopped strands are the fibers ranging from 3 to 50 mm and are cut from continuous strands. Chopped strand can also be laid down in a



random pattern to create a reinforcing mat designed to provide nondirectional reinforcement. These mats are available in a variety of thickness, usually expressed in weight per square meter. In order to hold the fibers together, a resinous binder is generally used, the type depending on the resin and molding process. In some cases, the mats are stitched or needled, instead of using the resin binder.

Chopped fiber lengths used in compounding SMC vary from 6 or 12 mm to 25 and even 50 mm. Increasing the fiber length improves molding efficiency. In molding, the short length fibers have been found to provide better compound flow. Actually, part designing and molding criteria will be the principal regulators of glass lengths required.

### 1.3 Resin-Glass Fiber Interface

Glass fiber required specialized treatments during the production process and subsequent use. Sizing or surface treatments are applied to the glass fibers. Each treatment, generally organic, provides some specific beneficial quality such as providing lubrication, protecting the individual filaments, holding the strands together, or providing compatibility with the resin system used in the manufacture of the glass-reinforced end product. These surface treatments generally can be classified as two basic types; textile sizings and reinforcement sizings (10).

Textile sizings are ordinarily used for treatment of fibers to be used later for manufacture of fabrics.

Reinforcement sizings are generally used to improve the bonding properties of the glass fiber with the resin system.

Sizing materials are two formulations of:

a. *Textile Size*; A complex starch-oil emulsion applied to fibers to be used for textile type applications (such as twisting, plying or weaving), and

b. *Reinforcement Size*; A chemical complex containing an organic resinous film former, a wetting agent, and a surface active agent applied to fibers intended for use in the reinforcement of resin systems and the so called *coupling agents*.

The coupling agents used in the chemical complex for reinforcement size are generally of two types: i) the chrome complexes ii) the silanes which have been developed for use with glass fibers (10).

Coupling agents are defined primarily as materials that improve the adhesive bond of dissimilar surfaces (11). But it may also involve better wetting, rheology and other handling properties. The coupling agent may also modify the interface region to strengthen the organic and inorganic boundary layers. The model structure shows the boundary of interface layer between the surface of matrix and the glass fiber as illustrated in Figure 1.4.



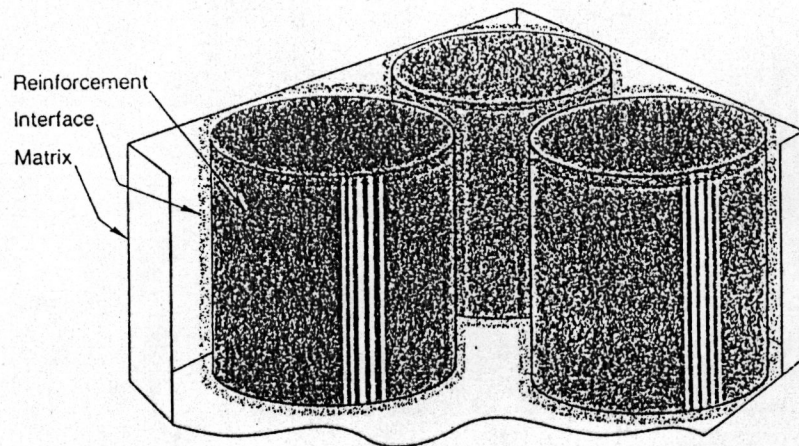


Figure 1.4 The model structure shows the boundary of interface layer between the surface of matrix and the glass fiber

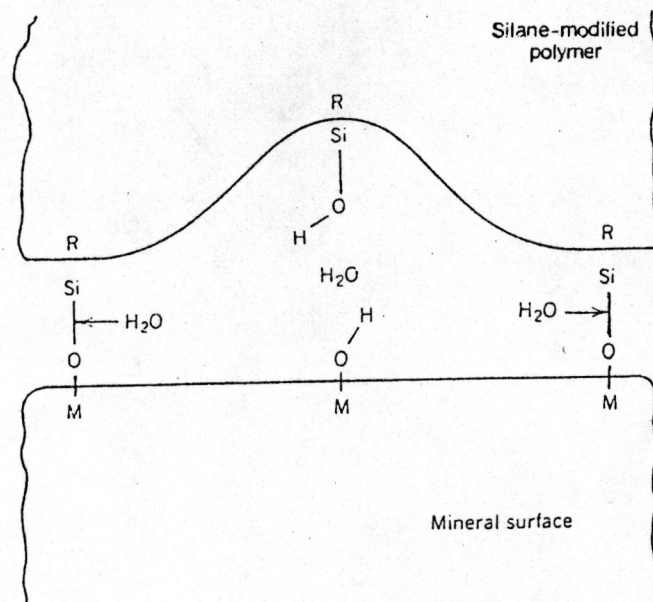


Figure 1.5 Idealized structure of a silane modified interface between matrix and reinforcement

The nature of adhesion of coupling agents is compounds contain both organic and inorganic groups; they bridge the interface between resin and reinforcement, as shown in Figure 1.5. Organofunctional silanes have R-groups that form covalent bonds with the resin, whereas hydroxyl groups form oxane bonds Si-O-M which bond to the mineral surface.

As the glass fibers have been used with unsaturated polyester resins. The coupling agents used consist of an inorganic component reacting with the glass surface and an organic component having at least good compatibility with the polymer matrix.

Silanes are the most common commercial coupling agents. They usually have the form  $X_3SiY$ , where X is typically a chlorine or alkoxy group and Y is the organofunctionality. These chemicals are usually applied from an aqueous solution to fibrous reinforcements. When applied to glass fiber, silanes hydrolyze, partially polymerize and bind to the glass by silicon-oxygen bonds. The solutions applied to the reinforcement are usually very dilute, only 0.01 to 2.0 wt%, to keep the highly reactive hydrolyzed product (silanols) from reacting with each other rather than with the glass.

The chemical reaction of silane coupling agent at the interface between the resin matrix and reinforcement was shown in Figure 1.6. Organo-silane coupling agents react with water in



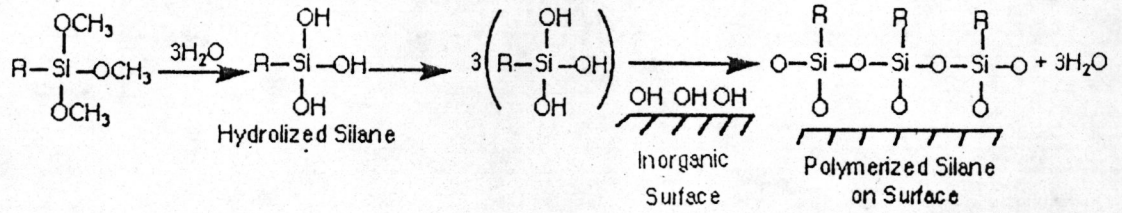


Figure 1.6 The chemical reaction of silane coupling agent.

Methacrylate  
silane

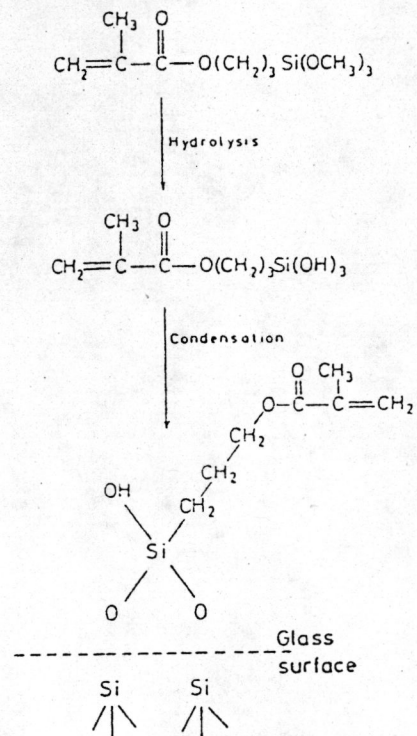


Figure 1.7 Reaction of gamma - methacryloxypropyl trimethoxy silane with the glass surface.

aqueous solution to form hydrolyzed silanes, which react with the surface of the inorganic reinforcement. The bound silanes polymerize, building up layers outward from the reinforcement with the organic functionality oriented into the matrix (12).

The silane coupling agent now most commonly used with unsaturated polyester resin is gamma-methacryloxy propyl-trimethoxy-silane, commonly known as methacrylato silane. This coupling agent gives glass fiber/polyester resin product higher physical properties, particularly flexural strength and the resistance to moisture is also improved. Figure 1.7 shows the reaction of this coupling agent with glass fiber (13).

However as glass fiber reinforcements have been used with other resins, new silane coupling agents have been introduced with specific reactivity for those resins. In general, the best coupling agents are those where the organofunctional group on silicon (Si) has maximum reactivity with the particular thermosetting resin during cure.



## 1.4 Formulation and Manufacturing Process of SMC

### 1.4.1 Formulation for SMC

A characteristic of SMC composition is shown in Table 1.1. This formulation is representative of the general type of SMC. It may be regarded as a starting point for the preparation of SMC in the experiment.

Table 1.1 A typical SMC Formulation

Material	Weight (part)
Resin : styrenated unsaturated polyester	100 parts
Catalyst : t-butyl perbenzoate	1 phr*
Release agent : zinc stearate	2 phr
Filler : calcium carbonate	50 phr
Thickener : magnesium oxide	2 phr

\* phr : parts per hundred of resin

#### 1.4.2 Manufacturing Process of SMC

Manufacture of SMC is a multistage process (Figure 1.8). The ingredients, shown in Table 1.1 except glass fibers, which are mixed into a paste, to be called as resin mix, is impregnated with chopped glass fiber, using special machinery to form sheets. These sheets are aged for several days to mature; molding produces the fabricated SMC products.

The sheet preparation is the most important step. It provides a mean to combine resin mix with glass fibers in a controlled manner. This step distinguishes SMC from other fiber-reinforced plastics, such as bulk molding compounds (BMC).

Figure 1.9 shows a schematic diagram of a sheet molding compound processing machine. The resin mix is first fed onto a carrier film, such as polyethylene. Glass fiber roving is chopped into desired lengths and uniformly deposited onto the moving layer of resin mix. Another layer of resin mix on a second carrier film is applied to the top of the chopped fibers. The resulting sandwich of resin mix and fibers between the carrier film is carefully kneaded by a series of rolls to impregnate the fibers completely with resin mix. The SMC is rolled up and allowed chemically to increase in viscosity (maturation). After maturation, all carrier film is removed, the SMC material is cut into pieces of specified size. It can be molded by compression molding. By application of heat and pressure cause the SMC to



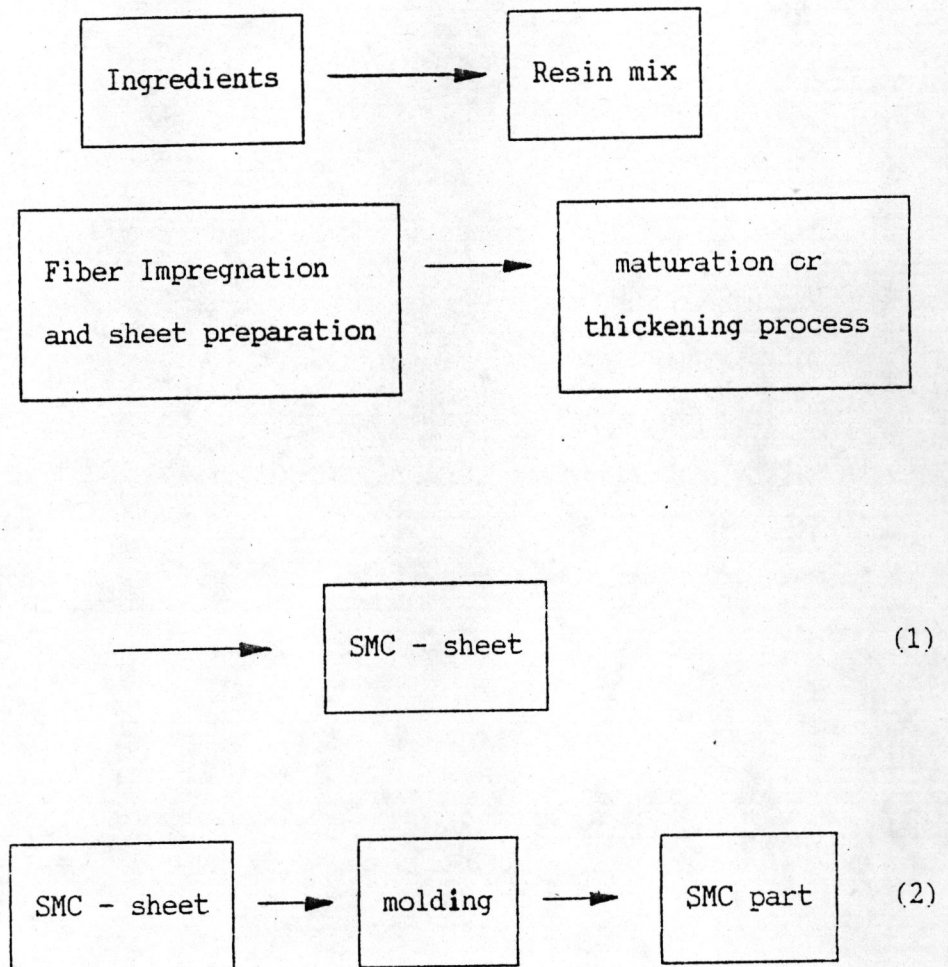


Figure 1.8 A multistage process of SMC

(1) Schematic diagram of SMC sheet preparation

(2) Schematic diagram of molding SMC part.

flow to all areas of the mold and cure or crosslinking takes place. The part is then removed from the mold (2).

The principal advantages of the SMC process :

- i) High-volume production.
- ii) Excellent part reproducibility.
- iii) Low labor requirement per unit produced
- iv) Minimum material scrap.
- v) Excellent design flexibility (from simple to very complex shapes).
- vi) Parts consolidation (ability to combine several features in one system).
- vii) Weight reduction.

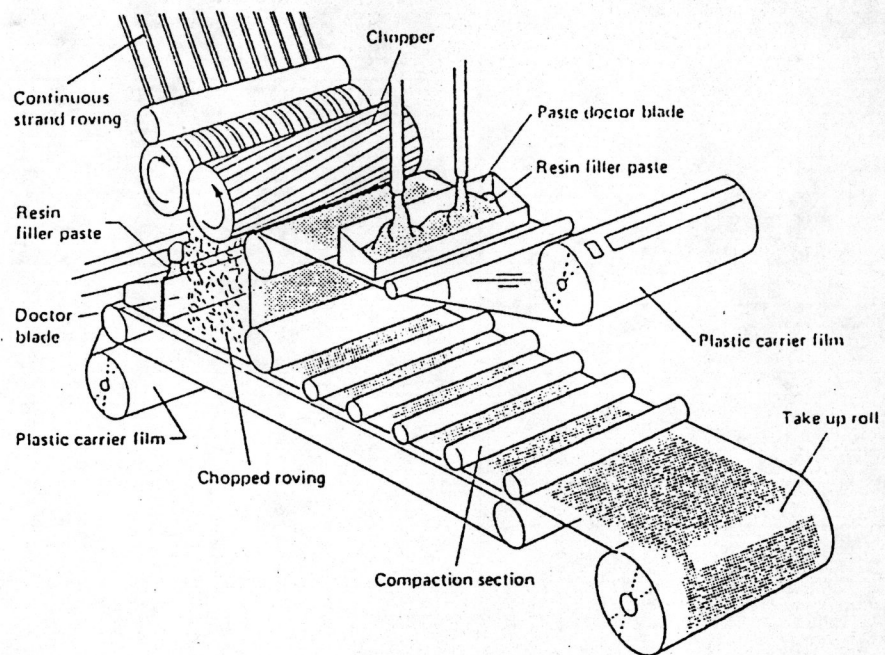


Figure 1.9 Sheet molding compound processing machine



### 1.5 Research Objectives

The main objectives of this research are :

i) to identify the relationship between compositions and mechanical properties of glass fiber and filler added to the polyester resin that forms the matrix of SMC fiber-reinforced materials;

ii) to study processing technique of SMC, sheet compounding and molding compound on a laboratory scale.

The additives are MgO as thickener and CaCO<sub>3</sub> as particulate filler. Both of these additives which are considered in formulating SMC, were studied in relation to behavior in term of flow properties with thickening time as a function of their compositions.

It is hoped that the compounding and processing would provide some in-depth in formulation of SMC reinforced plastics which is considered as a new technique in Thailand. This particular thesis does not intend to indicate any specific products derived from the formulations. However, further developments from the information obtained together with the existing techniques could be applied to the fabrications for several engineering products.