CHAPTER II

THEORY AND LITERATURE REVIEW

Sheet molding compound (SMC) is a polymeric composite material. The term SMC was adopted by the Society of the Plastics Industry (SPI) to denote a resin impregnated chopped-stand fiberglass in a dry sheet form (3).

Sheet molding compound was first prepared in the Federal Republic of Germany (FRG) by the Farbenfabriken Bayer Co. in the early 1960s. Its use spread quickly through Europe and Japan, mostly in the electrical and the communications industries, before any significant developments in the United States. In 1965, the U.S. Rubber Co. introduced an SMC under the trade name Vibrin Mat, and in 1966, the General Tire and Rubber Co. introduced Structoform. In the following years, Owens-Corning Fiberglass Corp. developed SMC systems containing improved glass roving and low shrinkage polyester resin. This development of so-called low profile SMC marked the beginning of high volume automotive application. During the last decade, the annual consumption of SMC in the automotive industry alone (include trucks) has grown from

50 x10^3 metric tons in 1975 to more than 120 x10^3 tons in 1985. Other applications range from aircraft parts to appliances, business equipment, and electrical components (3). However, the need for a faster cycle time, to complete with steel and other plastics, has created new challenges, as faster-curing formulations have traditionally been achieved at a sacrifice in surface smoothness (2).

2.1 Theory

2.1.1 Chemistry of SMC

The chemistry of SMC is complex because of the nature of the composite material. In general, an SMC is made up of a styrenated unsaturated polyester resin, a polymerization catalyst, an inert filler, metal oxide maturation agent(s), lubricant(s), a fibrous reinforcement, and a low profile thermoplastic polymer. It can be formulated in an almost infinite number of ways to produce materials with a wide range of properties for a variety of applications. A typical formulation is shown in Table 2.1.

The catalyst could be organic peroxide such as tert-butyl perbenzoate (TBPB), benzoyl peroxide (BPO), or dicumyl peroxide. The inert filler, usually CaCO$_3$, imparts stiffness. Magnesium oxide is often used as a maturation agent, and zinc stearate is a typical lubricant. Low profile agents are thermoplastic polymers, such as poly

(methyl methacrylate). They are added to improve surface smoothness by keeping shrinkage during molding to a minimum. These ingredients are mixed to form a paste which has the consistency of honey. It is mixed with chopped glass fibers in the next step and undergoes a maturation (or thickening) stage (usually several days) to produce a doughlike material which is more easily handled (3).

Table 2.1

A typical SMC formulation.

Material	Weight, %
Styrenated unsaturated polyester	24
Thermoplastic polymers	3
Filler, $CaCO_3$	41
Glass fiber, 12-50 mm	30
Polymerization catalyst	0.3
Maturation agent, MgO	0.7
Lubricant, zinc stearate	1

2.1.1.1 Unsaturated Polyester Resin

Unsaturated polyester resins in their commercial form are a mixture of an unsaturated polyester polymer, typically a solid with a vinyl monomer,

usually styrene. In the commercial resins, the ratio of the unsaturated polyester polymer to the styrene monomer is usually varied to accommodate the diverse applications that these materials find in the plastics industry. The final blend of the unsaturated polyester polymer and the styrene monomer is a viscous fluid.

In any application involving unsaturated polyester resins, the formation of the rigid three dimensional network that characterizes these materials comes from the free radical polymerization of the double bond functionalities of the unsaturated polyester resin and the styrene monomer. Different types of free radical initiators and catalysts are available for unsaturated polyester resins.

In the preparation of the unsaturated polyester resins, the types of anhydride and glycol play an important role in the final properties of the crosslinked network. Thus, the broad range of properties obtainable with unsaturated polyester systems makes them suitable for a wide variety of applications.

Technologically, unsaturated polyesters may be classified into two groups. Group A corresponds to unsaturated polyester resins for hand lay-up and spray-up. Applications of group A resin in fiberglass reinforced products are boats, swimming pools,

and water tanks. Group B corresponds to unsaturated polyesters for matched metal die molding. High volume production items such as automotive and appliance parts are commonly made in matched metal molds. For group B, a premixed molding compound known as sheet molding compound (SMC) or bulk molding compound (BMC) is commonly used.

The free radical initiators or cure systems employed in group A and group B unsaturated polyester resins are different. For group A, the cure process is usually referred to as a room temperature curing process. For group B, the cure process is usually referred to as a hot temperature curing process. Thus, the curing temperature determines what type of free radical initiator and/or catalyst should be used in a particular application (4).

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 the 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 (an

exothermic reaction). The crosslinking units as the chains form a three-dimensional network which consequently results in a cured polyester molding compound. In most case, 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 (5).

2.1.1.2 Catalyst

Consolidation, or curing, of the SMC is most commonly achieved by the application of heat and pressure. As previously noted, during the cure of thermosetting polymers, the molecule reacts with each other to form a more rigid network of crosslinked molecules. The SMC are cured at high temperatures, depending on their formulation or catalysts.

A wide variety of peroxide catalysts are available to cure polyester resin at elevated temperatures. There are more than 50 different organic peroxides and azo compounds produced commercially as free-radical initiators for the polymer and resin industry. Because most organic peroxides exhibit good solubility in styrene and do not release gaseous by-products on cure and because some can be induced to decompose at lower

temperatures, they are preferred over the azo initiators. For optimum results, the initiator half-life, molding temperature, resin viscosity, initiator concentration, promotor concentration, and initiator sensitivity to the formulated resin should be taken into account (6).

The selection of the free radical initiator is usually based on its half-life. Half-life is defined as the time in which half of the peroxide quantity decomposes at a given temperature in a defined solvent. The decomposition rate is of first order and is characterized by the following equation $dC/dt = KC$ where C is the concentration of initiator, t is the time, and K is the rate constant. For convenience, the stability of a peroxide in dilute solution is listed according to the temperature at which it has a half-life of 10 hours. The higher the temperature, the greater the stability of the peroxide. Thus, benzoyl peroxide, commonly used in a room temperature cure, has a 10-h half-life temperature at $73^{o}C$; whereas tert-butyl perbenzoate (TBPB), commonly used in a high temperature cure, has a 10-h half-life temperature at $105^{o}C$ (4). The optimum molding-temperature range with this catalyst is 140-150°C. Although higher temperatures can be used to effect shorter cure times. Similarly, the use of peroxides with lower decomposition temperatures can be used for similar purposes (6).

The curing agents vary in their

ability to promote cure. Therefore, the particular catalyst must be selected for a specific resin system depending on several factors including shelf life requirements, a curing temperature, and an acceptable molding cycle (7).

The specific requirements of the SMC process, however, limit this choice considerably. For example, the ideal catalyst should allow a long ambient-temperature shelf life for the sheet, a 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 the cycle time.

Over the years, the peroxyester t-butyl perbenzoate (TBPB) has come to be recognized as the workhorse catalyst for SMC. It provides adequate shelf lives, sufficient flow, and satisfactory cure times. With the advent of shorter stroke presses and the goal of 60-second cycle times, however, faster-reacting catalyst systems can be used since pregel is minimized with the faster press closing speeds (1). Table 2.2 lists some of the typical classifications of commercial peroxide catalysts that are available to cure the polyester resins at elevated molding temperatures (8). Note that the peroxides have significantly different 10-h half-life temperatures. In principle, half-life temperatures compare activity of one peroxide against another and therefore are often used as a basis for initial catalyst screening. For

example, a 'hot' catalyst with give a lower half-life temperature will give a lower gel time in the SMC process at elevated molding temperatures than a catalyst with a higher half-life temperature (1).

Table 2.2

Commercial peroxide classifications.

Peroxide type	Structure	10-h $t_{1/2}$, °C[a]
diacyl peroxides	$\underset{\text{RCOOCR}}{\overset{\text{O O}}{\parallel\ \parallel}}$	20–75
acetyl alkylsulfonyl peroxides	RSOOCCH₃ (with O above and below S)	32–42
dialkyl peroxydicarbonates	$\underset{\text{ROCOOCOR}}{\overset{\text{O O}}{\parallel\ \parallel}}$	49–51
tert-alkyl peroxyesters	$\underset{\text{R'COOR}}{\overset{\text{O}}{\parallel}}$	49–107
OO-tert-alkyl O-alkyl monoperoxycarbonates	$\underset{\text{ROOCOR'}}{\overset{\text{O}}{\parallel}}$	90–100
di(tert-alkylperoxy)ketals	ROO, R' / C \ ROO, R''	92–115
di-tert-alkyl peroxides	ROOR'	117–133
tert-alkyl hydroperoxides	ROOH	133–172
ketone peroxides	(ketone peroxide structures) + other structures	

^{a} $t_{1/2}$ = 10 h.

The type of peroxide initiators available, their sensitivity to induced decomposition, and associated application temperatures are listed in Appendix A, "Organic Peroxides as Polymerization Initiators" (9).

Reductions in cure time have been accomplished by combining the more stable t-butyl perbenzoate (TBPB) with a faster but less stable peroxide, e.g., t-butylperoctoate. This particular dual system has been used in SMC resin formulations to produce curing times of about 60-90 seconds at a molding temperatures of 150 to 160°C.

2.1.1.3 Filler

The fillers used in sheet molding compounds should be free of metal oxides or hydroxides which can cause uncontrollable thickening reactions. Commonly used fillers include:

a) Calcium carbonate ($CaCO_3$) : Calcium carbonate can be added in large amounts to the resin and still can maintain a processable paste (25-50,000 mPa-s). It assists in reducing shrinkage of the molded parts and in distributing glass reinforcement for better strength uniformity.

b) Hydrated alumina filler :
Hydrated alumina fillers are incorporated in SMC to provide flame retardancy while maintaining good electrical properties.

c) Kaolin clay: Kaolin clays are sometimes used in combination with $CaCO_3$ or hydrated aluminas. When added at 10 to 20% of the total filler weight, the clay serves to control viscosity in the resin paste, to promote flow, and to improve resistance to cracking in molded parts.
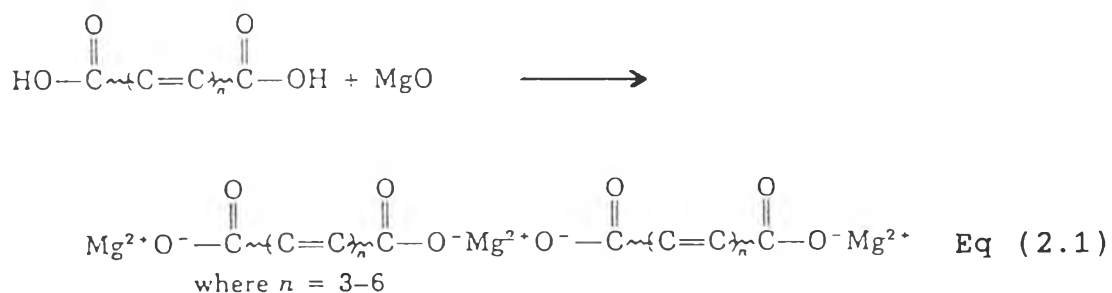
The calcium carbonates of various particle sizes and several types of clays have been used. The particle size of fillers affects properties of SMC, too. The smaller the particle size, the better the flow of the molding material and the improved surface appearance of molded parts.

The filler content of a given compound is indirectly proportional to the amount of reinforcement need to satisfy the mechanical property requirements. Often the reinforcement can be replaced with minimal effect on the general moldability of the compound. Fillers are also used to enhance the appearance of molded parts, promote flow of the glass reinforcement during the molding cycle, and reduce the overall cost of the compound (7).

Inert fillers are sometimes mixed with the resin in an effort to reduce cost. However, many fillers increase the viscosity to such an extent that with hand lay-up methods much more of the resin-filler mix is required to impregnate to mat. Since greater difficulty in working may also prolong processing time and there is invariably a marked drop in mechanical properties, care must be taken before making a decision whether or not to employ fillers (10).

2.1.1.4   Thickener

The majority of thickeners used in SMC are the oxides or hydroxides of calcium, magnesium, and zinc. They initiate the changes in the SMC mixture, converting into a manageable, reproducible molding material (7). The exact mechanism of maturation is not well understood.   The following reactions may take place to convert the viscous SMC paste to a doughlike sheet (3).

$$HO-\overset{\overset{O}{\|}}{C}\sim C=C\underset{n}{\sim}\overset{\overset{O}{\|}}{C}-OH + MgO \longrightarrow$$

$$Mg^{2+}O^--\overset{\overset{O}{\|}}{C}\sim C=C\underset{n}{\sim}\overset{\overset{O}{\|}}{C}-O^-Mg^{2+}O^--\overset{\overset{O}{\|}}{C}\sim C=C\underset{n}{\sim}\overset{\overset{O}{\|}}{C}-O^-Mg^{2+} \qquad \text{Eq (2.1)}$$
where n = 3–6

Although the rate and extent of thickeners used, certain organic amide thickening-control agents have been used to speed the thickening reaction and

to maintain the desired viscosity for long periods. Dual thickening of SMC has been achieved by using alkaline-earth oxides in combination with either isocyanates or certain metal halides. Because very low or very high viscosities are detrimental to the handling or molding of compound, it is extremely important to devise methods to control the amount of added thickening agent, One such method is based on calorimetric measurement (10).

2.1.1.5 Internal Mold Release

Zinc, aluminum, and calcium stearate are used at the 1-3% level with stearic acid about the same to reduce adhesion between the mold and the parts. An excessive amount of mold release agent can reduce the mechanical strength and cause an objectionable cosmetic appearance on the molded part surfaces (7).

2.1.1.6 Inhibitor

The addition of inhibitors to ethylenically unsaturated systems for the prevention of measurable amounts of polymer formation is widely practiced. However, in an unsaturated polyester SMC, they function other than to prolong storage life. They modify or retard the rate of cure to prevent crazing or cracking, which results from high exotherms, and to prevent undesirable changes in the gel time on long-term storage.

Inhibitors also greatly contribute to minimizing changes in gel time in the presence of other additives and they aid in reducing discoloration during processing.

Inhibitors used in unsaturated polyester resins are of two general classes, i.e., the various substituted phenolic derivatives and the quaternary ammonium salts. The mechanistic schemes for the inhibitory action of quinones and catechols have been elucidated. Inhibition is accounted for by the quinhydrone structure which can undergo equilibrium disproportionation to hydroquinone and quinone.

The use of hydroquinone, quinone, and their mono-and di-substituted derivatives is very common in the manufacture of unsaturated polyesters. Resorcinols and phenols are weak in their activity and, therefore, are used as auxiliary inhibitors. Other inhibitors, i.e., chloranil, nitrobenzene, or nitrotoluene, phenothiazine, and various aldehydes, generally are not use (11).

2.1.1.7 Reinforcement

The typical reinforcement of SMC has been glass fiber with a concentration of 15-30%. The fiber glass length can be varied from 1 cm up to any desired length depending on the end-use requirement. In

some case, continuous glass stand is introduced with the
chopped fiber for maximum strength in critical areas (7).

2.1.2 Manufacture of SMC

The manufacture of SMC is a multistage
process (Figure 2.1). The mixing stage involves the
preblending of resin, catalyst, filler, thickening agent,
and release agent. The ingredients, except for glass
fibers, are mixed into a paste, which is then impregnated
with chopped glass fiber, using special machinery to form
sheets. These sheets are set aside for several days to
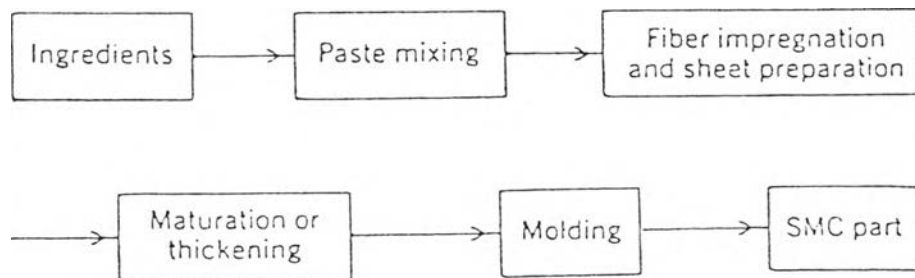mature or thicken; molding produces the fabricated
articles (3).

Figure 2.1 A flow diagram of a SMC manufacturing process.

The sheet preparation is the significant
step. It provides a way to combine a resin paste intimately
with glass fibers in a controlled manner. This step
distinguishes the SMC from other fiber-reinforced plastics
(FRP), such as bulk molding compounds (BMC). Figure 2.2

shows a schematic diagram of a sheet molding compound
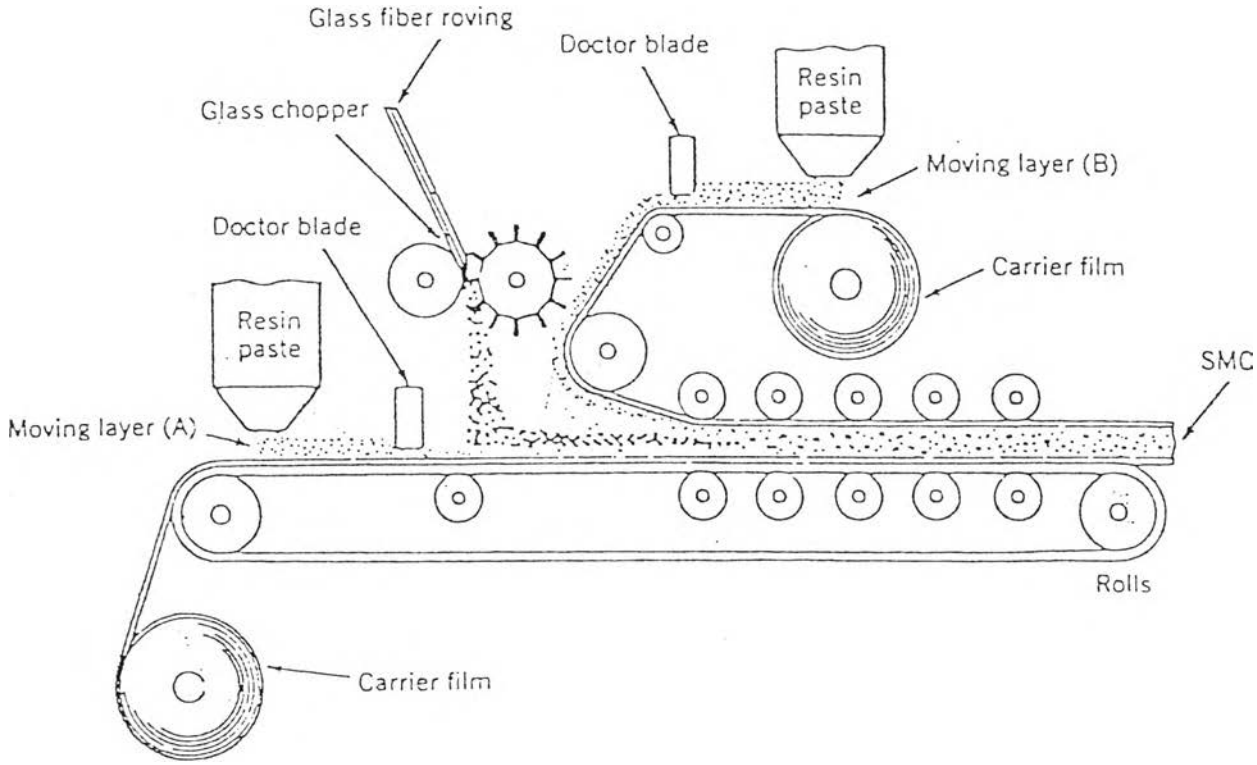machine.

Figure 2.2 Sheet molding compound machine.

The resin paste is first fed onto a carrier
film, such as polyethylene; it has a viscosity of about 5
to 80 Pa-s. Glass fiber roving is chopped into desired
lengths and uniformly deposited onto the moving layer (A)
of paste. Another layer (B) of resin paste on a second
carrier film is applied to the top of the chopped fibers.
The resulting sandwich of resin and fibers between the
carrier film is carefully kneaded by a series of rolls to
impregnate the fibers completely with resin. At this point,
the material has a viscosity of about 200 kPa-s (3). This

sandwich is carried though squeeze rollers to force the resin-filler into the mat and to control the ratio of resin-filler to mat. The sandwich passes through an oven to accelerate the thickening process or it may be rolled up and allowed to thicken in storage approximately 1 to 7 days (7).

A long-standing problem in SMC manufacture is the control of the production environment, allowing regulation of paste viscosity throughout the maturation period. The viscosity of the resin paste must be sufficiently low in the sheet preparation stage to obtain a good wet-out of the glass fibers. Furthermore, in the molding process the viscosity must be high enough to prevent fiber separation from the resin paste yet not high enough to prevent flow during molding.

The matured SMC is cut into pieces of a specified size. It can be molded by compression, transfer, or thermoset injection methods. Most SMC products are made by compression molding. The principal advantage of the SMC process, compared with other reinforced plastics manufacturing methods, is the ability to combine several features in one system. These include the potential for a high volume production, the capability to impregnate efficiently relatively long reinforcing fibers with resin without fiber degradation, and the ability to mold parts with complex shapes (3).

2.1.3 Cure Analysis of SMC in Molds

Compression molding is commonly employed in the fabrication of SMC into desired shapes. The process of compression molding of SMC normally involves four steps:

1) material preparation

2) molding filling

3) curing

4) ejection of parts and cool-down

The cure reaction of SMC is basically a radical chain growth copolymerization between the styrene monomer and the unsaturated polyester molecule. The theoretical consideration of this reaction has been studied by several researchers. Cure analysis of SMC molding has also been carried out by many researchers either experimentally or theoretically (12).

Unlike the processing of thermoplastics, the curing process of styrene-unsaturated polyester (UP) resins includes not only reaction kinetics but also gelation and network formation. Before the reaction, the resin is a viscous liquid. It becomes more and more viscous during the reaction. The increase in viscosity is caused by the formation of macromolecules. As a result of the crosslinkings on the multi-unsaturation points of the polyester molecules, the reacting system finally forms a

macro-network and then leads to an infinite viscosity. It is the so-called "gelation". The whole reaction, therefore, is separated into two stages: a pre-gel stage (i.e., before gelation) and a post-gel stage (i.e., after gelation).

In the pre-gel stage, the kinetics and the viscosity change are major parameters to monitor the reaction. One may reasonably conclude that the viscosity rise is kinetics affected because it is induced by the chemical reaction. However, the occurrence of gelation may be influenced by the phase miscibility between the resin phase and the formed macromolecule phase during curing. This phenomenon may determine the final morphology of the products. On the other hand, in the post-gel region, all the reactions occur in a "gel state" or a "solid state" for a vitrified sample. The sol-gel fraction would be an indicator of macro-network formation rather than the kinetics, because the latter shows the residual $C=C$ groups, including the pendant $C=C$ groups, on the polymer network structure, while the former shows the amount of reactants contributed to the polymer network (13).

In the actual SMC compression molding, material flow starts as the charge is placed on the bottom mold. The top mold is moved down rapidly until it nearly touches the charge surface in order to reduce heat conduction between the charge and the bottom mold. Heat conduction during this stage, called dwelling when the

charge is setting on the bottom mold, leading to a non-isothermal and asymmetric flow was respect to the midplane of the charge during compression molding. This may generate an asymmetric temperature profile and a non-uniform distribution of curing agent (i.e., catalyst and initiator) concentration through the SMC part, which, in case may result in a non-uniform curing pattern. In other words, the material near the bottom surface tend to react earlier than other locations. This phenomenon is called "dwelling effect".

Due to the complexity resulting form the interaction among mold filling, heat transfer and cure reaction, it is not easy to analyze the entire process as whole. Jyh-dah Fan and L. James Lee (12) assumed that the SMC molding can be broken into two sequential stages, i.e., flow and cure. At the flow stage, by assuming no significant cure reaction, momentum and heat transfer are the two major governing phenomena. The concentration of curing agent at different locations will affect the flow and heat transfer. At the cure stage, which starts after the mold has been filled, only cure reaction and heat transfer need to be considered. The distribution of temperature and curing agent concentration resulted from the flow stage serve as the initial conditions of the cure stage.

Since SMC resins gel at very low

conversions, a premature gelling (i.e., a scorch problem) may occur if the cure reaction starts during mold filling. This may result in a poor surface finish of molded parts and may sometimes cause incomplete mold filling. Therefore, a SMC compound must be designed in such way that no cure reaction may occur during mold filling. This is achieved by controlling the type and concentration of catalyst and inhibitor in the curing agent.

2.2 Literature Review

The principal shortcomings of molded SMCs today include problems related to surface finish, mechanical property variability, and cycle time. Considerable research has been devoted to improving surface quality and finish; an in-mold coating process has been used in 1978. Thickening by iso-cyanate reactions or interpenetrating thickening processes have been described. In 1979-1981, improved press control and new mold heating design have also been proposed. In 1980-1983, extensive efforts by materials and equipment suppliers have been reported to reduce the cycle time and improve productivity. In 1984, a novel compacting method improves physical properties, including the tensile strength, isotropy, and surface characteristics. During 1986-1987, the average molding-cycle time for SMC is 3-4 minutes, which is the highest allowable in automobile production rates (3). Continuing advances in low-profile SMC technologies have been made

possible exceptionally smooth surface automotives and truck body panels. However, the need for faster cycle times, to complete with steel and other plastics, as faster-curing formulations have traditionally been achieved at a sacrifice in surface smoothness (2).

Since 1980, t-amyl analogues of t-butyl peroxyketals and some peroxyesters have been introduced into use with SMC/BMC formulations. These catalysts are said to offer somewhat higher reactivity at lower temperatures as well as thorough cures for maximum strength properties and better surface finishes.

As showed in Table 2.3, a new t-amyl perketal, Lupersol 431-80B, offers an approximately 10% shorter cure time in a filled SMC resin than does its t-butyl counterpart, Lupersol 331-80B (7).

A t-amyl peroctoate, Lupersol TA75-M57, which was introduced in 1980 shows a 25% reduction in cure time versus its t-butyl equivalent (14).

Although t-butyl perbenzoate (TBPB) is widely used, a type of t-amyl derivative is now on a development stage (15, 16). The latter is basically more active than the former, as the t-amyl derivative provides about a 20% faster cure at an equal amount of concentration in low profile SMCs.

Table 2.3

Comparison of activity of the t-amyl vs t-butyl peroxides

at mold temperatures of 120 and 150°C[a].

Catalysts	Concentration (phr)	SPI gel (min)	Exothermic cure (min)
t-butyl perbenzoate[b]	1.0	2.0	2.7
t-butyl perketal (Lupersol 331-80B)[b]	0.84	1.2	1.8
t-amyl perketal (Lupersol 431-80B)[b]	0.77	1.0	1.6
t-butyl peroxydi- carbonate (Lupersol TBEC)[b]	1.27	1.5	2.2
t-butyl perbenzoate[c]	1.0	6.0	7.2
t-butyl peroctoate[c]	1.12	1.0	1.6
t-amyl peroctoate (Lupersol TA75-M75)[c]	1.57	0.6	1.2

[a] Data provided by Lucidol Division, Pennwalt Corp. Owens-Corning, as E-4297 SMC Resin; all contain 100 phr of calcium carbonate, all catalysts contain an equal amount of total active oxygen concentration.

[b] Molding temperature, 150°C.

[c] Molding temperature, 120°C.

A unique class of nonperoxide initiator is also introduced to the FRP processing especially in the SMC molding. Azo catalysts are one type of this class (14). Even though azo initiators are more expensive than standard peroxides, they are more attractive in greater stability, safety and uniform cure. Mixing azos with perketals of higher half-life may result in a longer pot life of the perketal with the faster cure, typical of t-butyl peroctoate (16).

A new type of t-butyl peroxyester, Trigonox BPIC, a so-called t-butyl peroxy isopropyl carbonate was introduced by Noury Chemical Corp.(15, 16). It has a 10-h half-life temperature of about 97°C, a little faster than t-butyl perbenzoate (TBPB). This is said to provide a more thorough cure during high-temperature molding and lower styrene residuals.

Trigonox T is also being introduced to the SMC/BMC and prepackage molders, besides it has been used mainly in other applications. It is said to reduce styrene residuals and prolong shelf lives (16).

Two more SMC/BMC initiators have been presented by Azetc Chemicals. T-BCH is an 80% solution of perketal blended with t-butyl peroctoate. Strong points of this solution include thorough cures, long pot lives, and good cost performance. The other initiator is a liquid dialkyl

peroxide that is said to give eager flow times for filling complex molds. Its 10-h half-life temperature is 120°C. It is called 2,5-Di for short (16).

However, the goal for reducing the part cycle time of SMC today is the 60 seconds cycle time. A wide variety of fast-reacting catalysts is variable to obtain a gel time of under 60 seconds in a vinyl ester SMC. The Dual catalyst was found to be more effective in reducing the gel time while still providing an acceptable shelf life (1).

D.A. Babbington and J.H. Enos (1) has also studied a dual-catalyst system in the SMC. To further reduce the cure time over what can be obtained with a single heat-activated catalyst, dual-catalyst systems are often employed. One of the more common SMC catalyst combinations today is a so-called "hot" catalyst like t-butyl peroctoate (TBPO) with a half-life temperature of 74°C, and it is used in conjunction with t-butyl perbenzoate (TBPB). Various combinations of these two catalysts were investigated (1). The dual-catalyst system between the TBPO and TBPB was indeed found to be faster than the TBPB alone. However, the disadvantage of the "hot" catalysts such as TBPO is a drop in the shelf life of the sheet. The viscosity measurements were made over time for B-staged SMC pastes with these catalyst combinations. As shown in Figure 2.3, the compounds containing the higher levels of the TBPO catalyst had shorter shelf lives, as anticipated (1).
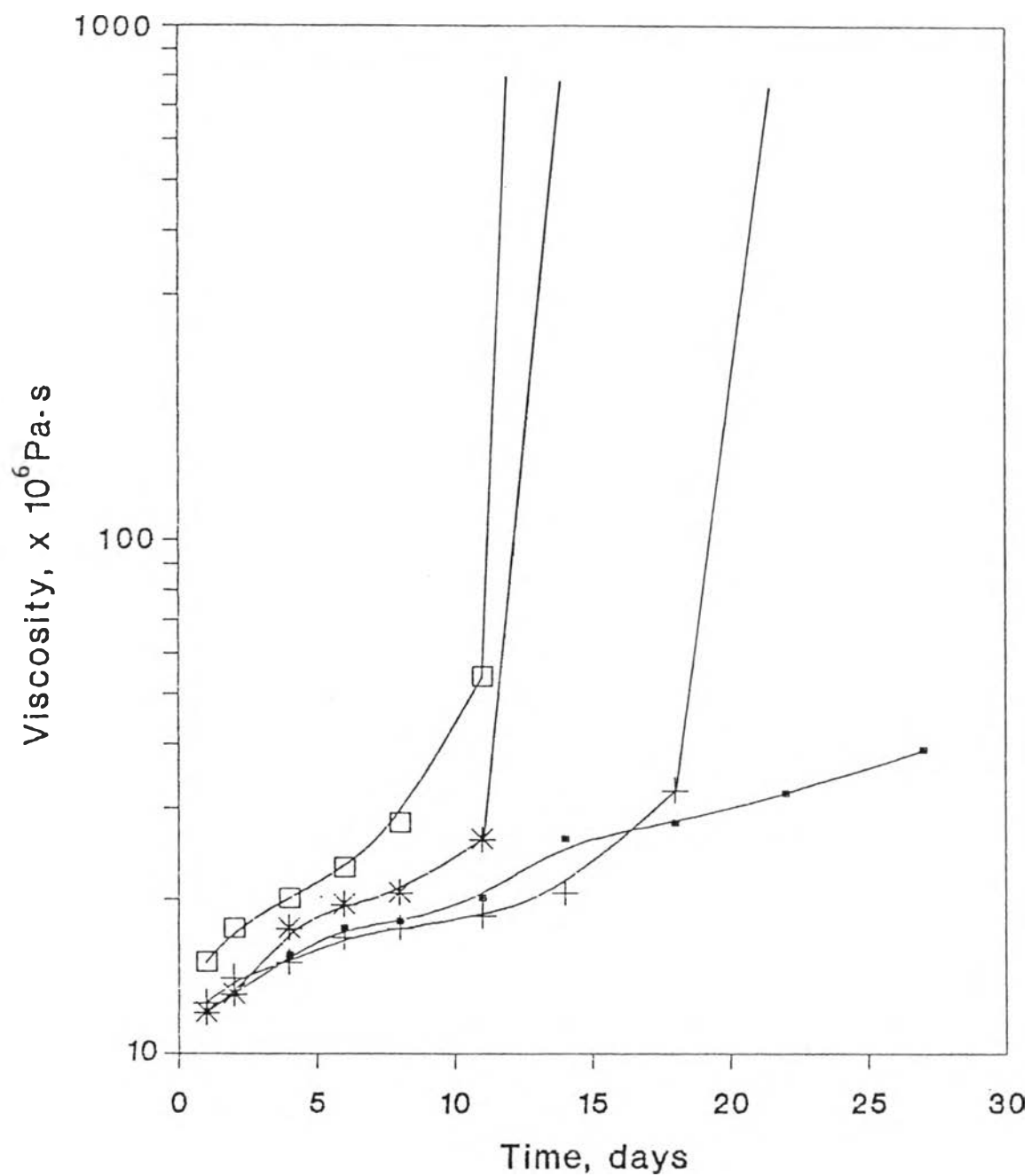
Figure 2.3 Viscosity of B-staged pastes, formulation: 100
phr Derakane 790; 120 phr $CaCO_3$ filler; 1.3 phr
MgO paste; 4 phr zinc stearate, tested at 25°C.
(――― 1 phr TBPB; ―+― 0.5 phr TBPO, 1.5 phr
TBPB; ―*― 1.5 phr TBPO, 0.5 phr TBPB; and
―□― 2 phr TBPO.)

Designing a catalyst system for the SMC, therefore, requires caution. A compromise in the shelf life of the SMC compound must be balanced by a reduction in gel time. With this trade-off in mind, additional dual catalysts were screened to find a system that would provide the best balance of shelf life and gel time. Peroxyketal catalysts, which had been reported as giving good room-temperature pot lives, were included in the screening. And a formulation containing parabenzoquinone (PBQ) was also included since it is commonly added to the catalyst package to extend the shelf life of the compound. Results of these combinations are shown in Figure 2.4. The only significantly reduced shelf life appeared to be for the formulation containing the highest level (1 phr) of the t-butyl peroctoate (TBPO) in conjunction with the peroxyketal catalyst.

Although a compromise must be made in the SMC gel time and shelf life selected, through a proper choice of the catalyst system, this compromise becomes less severe.
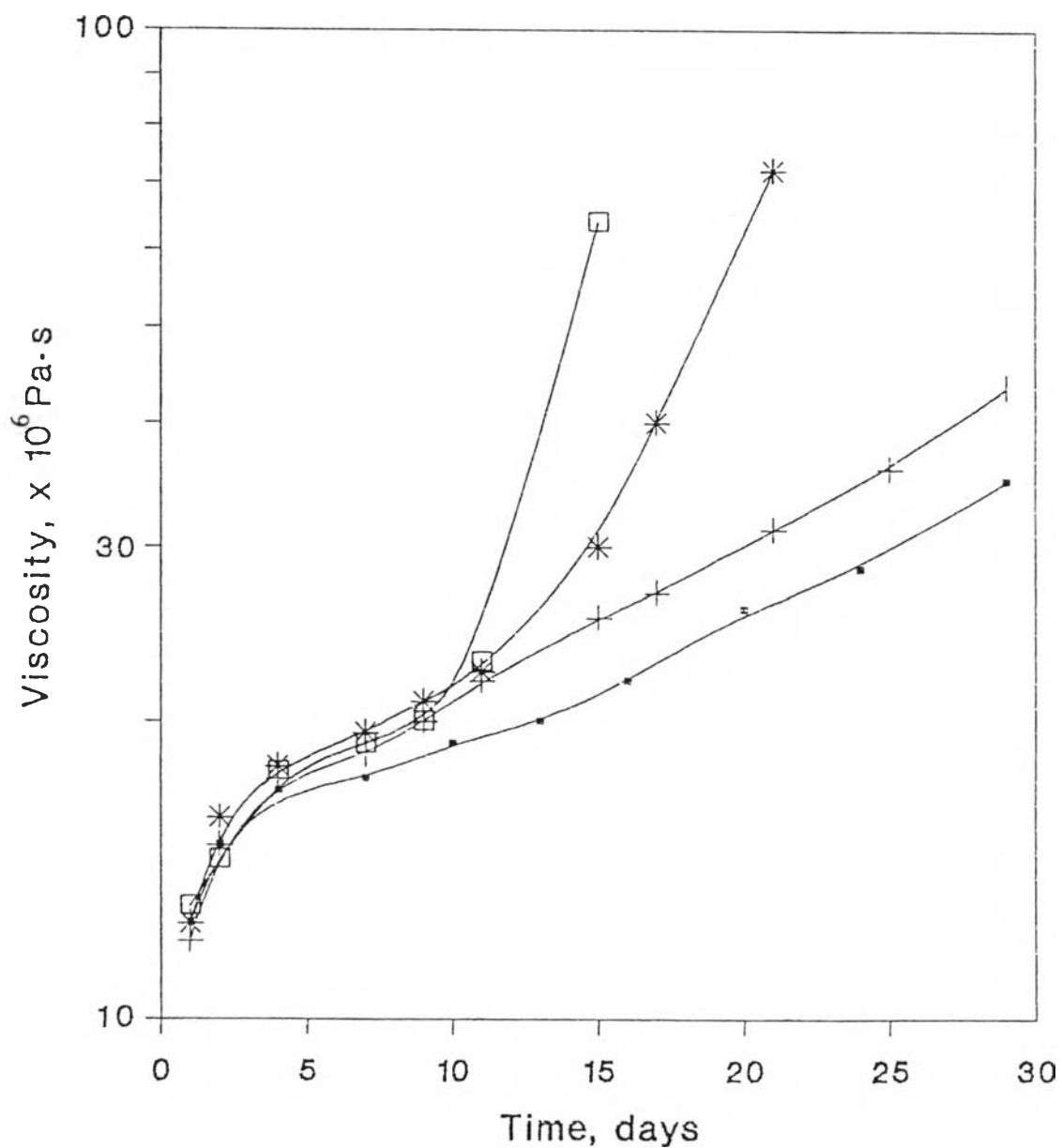
Figure 2.4 Viscosity of B-staged pastes, formulation: 100
phr Derakane 790; 120 phr $CaCO_3$ filler; 1.3 phr
MgO paste; 4 phr zinc stearate, tested at 25°C.
(—— 1 phr TBPB, 0.2 phr TBPO, 0.025 phr PBQ;
—⊢ 1.5 phr DTBC, 0.5 phr TBPO, 0.025 phr PBQ;
—⁕— 1.5 phr DTBC, 0.5 phr TBPO; and —⊟—
1.0 phr DTBC, 1.0 phr TBPO.)

In the final analysis (1), catalyst performance in the end user's plant is specific to the molding conditions employed. For this reason, a molding study was undertaken with a vinyl ester-resin SMC to determine the function of the fast catalyst combinations such as behavior and its sensitivity to process variables. According to the SMC and catalyst formulations shown in Table 2.4, the SMC compounds were prepared.

Table 2.4

The SMC formulation.

Formulation	Concentration (phr)
Vinyl ester resin (Derakane 790, Dow)	100
Calcium carbonate	120
Magnesium oxide slurry (40% MgO solids)	3.25
Zinc stearate	4
Catalyst[a]	Varies
Glass content	32 wt.%

[a] Catalyst formulations:

Formulation 1 contains 1.0 phr TBPB; 0.2 phr TBPO; 0.025 phr PBQ.

Formulation 2 contains 1.5 phr DTBC; 0.5 phr TBPO.

Formulation 3 contains 1.5 phr DTBC; 0.5 phr TBPO; 0.025 phr PBQ.

Formulation 4 contains 1.5 phr DTBC; 0.3 phr TBPO.

Formulation 5 contains 1.5 phr DTBC; 1.03 phr TBPO.

The effects of demold time and mold coverage on pregel are noted. Lower mold temperatures were found to give the least pregel. Higher mold coverage resulted in more severe pregel. As demold time was increased, the amount of pregel decreased.

Molded panels were also visually rated for effects of delaminations, defined as "blistering" of SMC sheet due to insufficient cure. Delamination was quantified for panels by measuring the longest distance inside each delamination and totaling these distances. As expected, the demold time was found to have the greater influence on controlling the formation of delaminations. This was expected earlier since delamination as defined is caused by the part being insufficiently cured when the tool is opened. Increasing the demold time remedies this occurrence.

Mold temperature was also found to indirectly affect formation of delaminations by controlling cure rate in the part. A higher mold temperature will hasten cure in the part, minimizing the delaminations formed.

Physical properties were tested on the five formulations for the SMC test panels fabricated under the same process conditions and with a 60 seconds demold time (1). Table 2.5 shows the results as compared to the sample of formulation 1 in Table 2.4 fabricated with a mold-close

time of 3 minutes. Again little difference was seen between
the physical properties, indicating that the 60 seconds
demold time was not detrimental.

Table 2.5

Effect of catalyst type on physical properties.

Mixture tested	Flexural stress, MPa		Flexural modulus, MPa	
	Longitudinal	Transverse	Longitudinal	Transverse
1[a]	160.4	207.9	9,310.3	10,206.9
2[a]	153.3	180.5	9,379.3	9,517.2
3[a]	140.1	191.0	8,413.8	10,206.9
4[a]	150.3	174.5	9,172.4	9,034.5
5[a]	179.7	182.0	9,586.2	9,862.1
1[b]	176.1	172.7	9,862.1	10,137.9

[a] Demold time equals 60 seconds; mold coverage equals 65%;
mold temperature equals (150°C).

[b] Demold time equals 3 minutes; mold coverage equals 65%;
mold temperature equals (150°C).

In conclusion, critical variables in the SMC
process that cause pregel and delamination have been
defined and documented for five catalyst formulations.
Formulation 1 containing the TBPB was the slowest and gave
the most severe delaminations for the process conditions

tested. Formulation 5 containing the 1 phr TBPO in conjunction with the peroxyketal had the most severe pregel as well as the shortest shelf life. The formulation containing the lower TBPO levels, balanced with the peroxyketal, gave the best compromise in gel time and shelf life. A wide variety of fast-reacting catalysts is available to obtain a gel time of under 60 seconds in vinyl ester SMCs. Dual catalysts were found to be more effective in reducing the gel time while still providing an acceptable shelf life. A compromise between gel time and shelf life must always be made, although through the proper choice of the catalyst system this compromise becomes less limiting (1).

Currently, the production molding of thousands of parts at a commercial installation has proven that SMC molders can save 13-17% in cycle time through a closed-loop press control based on an in-mold dielectric monitoring (17). An ICAM-1000 dielectrometer with SPC software has been used on a 2000 ton press molding a "consumer product" measuring 120 x 150 cm and 0.32 cm thick at an undisclosed customer. The system uses the in-mold dielectric sensing to detect when a full cure has occurred and then signals the press to open, rather than waiting for a timed interval. The system adjusts automatically for random variations in mold temperature, charge placement, or material uniformity.

In this case a manual press timer set for a 60 seconds cure had yielded 100% good parts. But the dielectrometer revealed a standard deviation of 5 seconds and an average actual cure time of 50 seconds. Thus, by controlling the press according to the actual cure profile on each cycle, an average of 10 seconds was saved, while still ensuring consistent part quality. In fact, the system automatically lengthened the mold-closed time in one instance when a platen heater was accidentally turned off, thereby avoiding production of scrap parts (17).