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Application of factorial design to SMC viscosity build-up

I.-Chung Tung

Department of Mechanics and Materials Science, Rutgers University, Piscataway, NJ 08854, USA

SUMMARY

The thickening behavior of SMC varies with formulation and operating conditions. During the SMC compounding process, alkaline oxides such as MgO, $Mg(OH)_2$, CaO, $Ca(OH)_2$ are added to the formulation to yield the viscosity build-up from a flowable paste to a semi-solid sheet. The thickening curve of SMC can be divided into three stages: 1. The initial thickening period for the wetting process, 2. The middle thickening rate period for viscosity increasing, 3. The final viscosity period for the molding process. By means of factorial design with an appropriate objective set-up, one is able to define the influence of each factor on thickening curves. Combined with the experimental work on some individual factors, the maturation control system can be further understood and the proper thickening rates can be obtained.

INTRODUCTION

Sheet molding compound, SMC, is a unique molding compound which takes advantage of a thickening process prior to molding. Through control of the thickening reaction, SMC possesses the following benefits which are not easily or simultaneously attainable in other molding compounds:

1. the ability to load a high content of reinforced fibers and fillers.
2. the ability to mold thick and wide parts.
3. the flow distance is short during molding thus avoiding fiber breakage and tending to keep fibers in an isotropic array.

In order to accomplish the above objectives, the thickening process from compounding to fiber wetting to molding must be carefully controlled as indicated below:

1. At the early stage of the thickening process, the viscosity should be low enough for thorough mixing of resin/fillers on the SMC machine and the time should be long enough for complete wet-out of glass fibers or carbon fibers.
2. An appropriate rate of increase in viscosity until the desired viscosity is reached.
3. The maintainance of this desired viscosity for a long period of time is essential to facilitate processing and to avoid waste of materials caused by too high of a viscosity.

A lot of research has been carried out on SMC thickening behavior which is primarily concerned with the evaluation of various kinds of thickeners, thickening control agents, and other components of various formulations on their ability to form an appropriate thickening behavior. However only I-Chung studied their effects on thickening curves(1). The present work is the study of the effects of some factors on thickening curves using factorial design with the aim of further understanding SMC maturation and thus rendering a better control of the thickening process.

FACTOR SELECTION AND OBJECTIVE SET-UP FOR FACTORIAL DESIGN APPROACH

1. Factor selection

A typical SMC formulation, as shown in Table 1, includes various kinds of organic materials possesing different magnitudes of effects upon thickening behavior. It is convenient to classify the factors that affect thickening behavior during SMC process in three categories:

(1) Intrinsic properties of materials: includes acid number, molecular weight, hydroxyl number, and particle size, particle shape, surface treatment of fillers etc.

(2) The amount of each component added: includes all components in a formulation.

(3) Processing conditions: includes temperature, humidity, evaporation of styrene, mixing style etc.

Table 1: SMC paste formulation

Cpmponents	Parts by weight
Polyester resin RLCG	60
Low profile agent LP-40A (Union Carbide Co.)	30
t-Butyl-Perbenzoate	1.5
Zinc Stearate	2
Calcium carbonate	(+):180--(-):160
Magnesium Oxide	(+):1.8--(-):1.6
Oleic acid	2
Oleic acid/Phthalic Anhydride	(+):4--(-):2

For SMC compounders, in the manufacturing process there is no need to consider the intrinsic properties of materials to complicate the analysis of thickening behavior. Therefore by taking the viewpoints of compounders, these intrinsic properties are omitted in this work.

In SMC processing, in addition to thickening, it is necessary to consider the low profile properties, the needed mechanical strength, the desired inflammability, or any other needed material properties at the same time. Hence the added amounts of initiator and styrene are determined by the curing system, and the amount of flame retardant is determined by the desired inflammability. As a consequence, it is natural to choose the added amount of thickener, thickening control agent, and calcium carbonate to be the factors that affect thickening curves.

The water content in SMC compound has a very significant effect on thickening behavior as indicated by Horner and Brill(2). A low water content is preferable, whereas a high water content leads to a slight decrease in the mechanical strength (cracking) and yields undesired effects on thickening behavior. If the content of water trapped from the atmosphere is adequate, there is no further need to add water. It should be noted that in this paper the water content is not selected as a variable in the thickening analysis.

On account of process conditions and in order to simplify the analysis, temperature is chosen as the only factor for analysis, with humidity and mixing style being fixed. In SMC processing, temperature has the most significant influence on the thickening curve when compared to humidity and mixing style. Therefore, in this experiment, the studied factors are thickeners, thickening control agents, calcium carbonate and temperature.

2. Objective set-up

Due to the characteristics of SMC thickening curves, a thickening curve can be divided into three stages: (1) the initial thickening period for the wetting process, (2) the middle thickening rate period for proper increase of viscosity, (3) the final viscosity period for the molding process.

For the above division of a thickening curve, TI is set as the time from the completion of mixing to the loss of wetting, TM as the time from TI to the attainment of the moldable viscosity, VF as the average viscosity for the first six days after the moldable region is reached, and VF1 and VF2 are the upper and lower limits of viscosity at the moldable region respectively. By using these definitions, the requirements for the thickening process can be expressed as follows:

(1) TI must be long enough for completion of the wetting process.

(2) TM should be as small as possible to decrease the storage pressure.

(3) VF should be maintained at the modable viscosity level (the viscosity level between VF1 and VF2) for as long as possible.

These statements are schematically shown in Fig. 1.

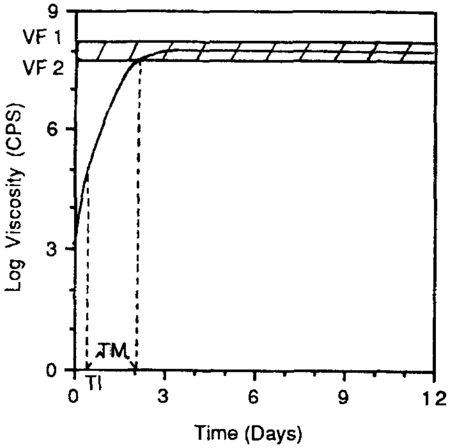
The objective set-up for this experiment, by fabrication experience, the values of TI, TM, and VF in this work are set as follows: (If the fabrication environment differs from this experiment, TI, TM, and VF can have different values.)

(1) TI has to be more than 30 minutes (TI > 30).

(2) TM should approach zero, that is, the lowest possible TM is desired. (TM → 0)

(3) VF1 is 8.11 and VF2 is 7.69. (VF1=8.11 and VF2=7.69, the viscosity set by the natural logarithm.) In other words, the value VF should be maintained between 8.11 and 7.69 for a long period of time.

Fig. 1 : Schematic illustration of the objective set-up



EXPERIMENTAL PROCEDURE

1. Thickening test

Two methods were employed to survey thickening behavior. One was the resin base type and the other one was the paste base type.

(1) Resin base type

The thickener or the other fillers were put into the resin directly and mixed by the Cowles-type mixer until the fillers were completely dispersed in the resin. Then thickening was monitored regularly with a Brookfield RVF viscometer using spindle #5 at 20rpm and 2rpm, spindle #7 at 2rpm and 0.5rpm, and with a Brookfield HBT viscometer using TF spindle at 1rpm and 0.5rpm.

(2) Paste base type

The resin base, the initiators, the release agent, and the thickening control agent were put into a 500ml beaker and mixed with the Cowles-type mixer until the fillers were completely dispersed in the resin. Then calcium carbonate filler was added gradually with agitation until a consistent paste was obtained. Afterwards, the thickener MgO was added to the paste and mixed further for about 2 minutes. Then thickening was monitored regularly with a Brookfield HBT viscometer using TA spindle at 5rpm and 0.5 rpm, and TF spindle at 1rpm and 0.5rpm.

2. The determination of the factor levels

First, a series of formulations were made to produce a set of thickening curves that meet our requirements as described in the objective set-up. From this data, as shown in Table 1, the high (+) and low (-) content levels of each factor were set far apart so that their effects could be clearly larger than experimental errors.

3. Data analysis

In this experiment, 8×10^4 cps (TA spindle at 5rpm) was taken as the viscosity of loss of wetting and the moldable region was from 5×10^7 cps (TF spindle at 1rpm) to 1.3×10^8 cps (TF spindle at 0.5rpm).

From the data obtained by the resin base type procedure, log viscosity versus time graphs were plotted.

From the data obtained by the paste base type procedure, the curve fitting method was used to plot thickening curves and to calculate TI, TM , and VF values. These thickening measurements provided a series of curves and the average of several calculated values of TI, TM, and VF.

4. The computation of effects

The effects were computed by a specific procedure as stated in reference(3). They represent the differences in the responses at the high and low content levels of the factors. From this computation, each factor's main effect on thickening and its interactions with other factors can be estimated. These calculated results can be used for the setting up of a prediction model for TI, TM and VF if the curvature of the responses is not large in the experimental region.

RESULTS AND DISCUSSION

In the SMC compounding process, the thickening behavior is very sensitive to the amounts of the additives, especially thickeners, thickening control agents, calcium carbonate and styrene. Weighing and adding the additives have to be carefully performed since any slight difference in weight can cause large change in thickening level.

From the computation of factorial design using two content levels, there are two mathematical model equations obtained as follows:

(1) According to the experimental design pattern given in Table 2

$$TI = 38.88 - 6.13\ X_1 + 5.13\ X_2 - 1.38\ X_1X_2 - 9.875\ X_3 + 2.63\ X_1X_3 + 0.13\ X_2X_3 - 1.13\ X_1X_2X_3 \quad \text{------------------------} \quad (1\text{-}1)$$

$$TM = 202.55 - 20.11\ X_1 - 22.16\ X_2 - 8.36\ X_1X_2 - 108.44\ X_3 + 7.29\ X_1X_3 + 11.09\ X_2X_3 + 4.24\ X_1X_2X_3 \quad \text{------------------------} \quad (1\text{-}2)$$

$$VF = 7.99 + 0.23\ X_1 + 0.09\ X_2 + 0.1\ X_1X_2 + 0.14\ X_3 + 0.07\ X_1X_3 + 0.05\ X_2X_3 + 0.02\ X_1X_2X_3 \quad \text{------------------------} \quad (1\text{-}3)$$

(2) According to the experimental design pattern given in Table 3

$$TM = 94.76 - 29.37\ X_1 - 34.25\ X_2 - 11.2\ X_1X_2 - 242.89\ X_4 + 25.43\ X_1X_4 + 27.77\ X_2X_4 + 13.2\ X_1X_2X_4 \quad \text{------------------------} \quad (2\text{-}1)$$

$$VF = 8.02 + 0.15\ X_1 + 0.06\ X_2 + 0.04\ X_1X_2 + 0.29\ X_4 - 0.01\ X_1X_4 + 0.02\ X_2X_4 - 0.04\ X_1X_2X_4 \quad \text{------------------------} \quad (2\text{-}2)$$

where

TI= the response of the time of the initial thickening period.

TM= the response of the time of the middle thickening period.

VF= the response of log the final average viscosity.

Table 2 : Experimental design

Variables Order	X_1	X_2	X_3	TI	TM	VF
1	-	-	-	52min	178.4hr	7.92
2	+	-	-	35min	159.9hr	7.96
3	-	+	-	63min	163.6hr	7.90
4	+	+	-	45min	120hr	8.02
5	-	-	+	25min	58.07hr	7.94
6	+	-	+	23min	49.37hr	8.03
7	-	+	+	40min	48.87hr	7.95
8	+	+	+	28min	31.93hr	8.16
Center point				33 30	79.2 82.65	7.96 7.98
				31 29	86.32 78.32	7.95 7.96

* Temperature : 24 °C
where

$S^2_{pool}(TI) = 4.32$ Curvature (TI) = 8.13

$S^2_{pool}(TM) = 1.52$ Curvature (TM) = 19.62

$S^2_{pool}(VF) = 6.56 \times 10^{-6}$ Curvature (VF) = 0.02

Table 3 : Experimental design -- including temperature

Variables Order	X_1	X_2	X_3	X_4	TM	VF
1	-	-	-	-	178.4hr	7.92
2	+	-	-	-	159.9hr	7.96
3	-	+	-	-	163.6hr	7.90
4	+	+	-	-	120hr	8.02
5	-	-	-	+	45.83hr	8.04
6	+	-	-	+	38.51hr	8.11
7	-	+	-	+	36.29hr	8.08
8	+	+	-	+	16.65hr	8.15
Center point					74.87 76.62	8.02 8.04
					73.62 73.85	7.98 8.01

* Calcium carbonate : 160 gram

Temperature X_4 — (+) : 34 °C (–) : 24 °C
where

$S^2_{pool}(TM) = 2.28$ Curvature (TM) = 26.52

$S^2_{pool}(VF) = 9.82 \times 10^{-6}$ Curvature (VF) = 0.01

Xj=Factor level -- [Xj(+)+Xj(-)]/2.
j=1 represents magnesium oxide.
j=2 represents the thickening control agent.
j=3 represents calcium carbonate.
j=4 represents temperature.

The above equations show the variations of responses of TI, TM, and VF between the high and low content levels of each factor. The coefficients represent the magnitudes of factor effects.

In view of these equations, the following information can be obtained:

In condition (1), the thickener increases TM but decreases TI and VF. The thickening control agent increases TI and VF but decreases TM. Calcium carbonate increases VF but decreases TI and TM.

In condition (2), the thickener, the thickening control agent, and temperature all decrease TM and increase VF, but temperature has the largest influence on thickener curves.

Referring to the above information, it can be seen that the thickening control agent can prolong the time of the initial thickening period, increase the middle thickening rate, and produce a positive effect on the needed thickening behavior.

The thickening control agent in this experiment is a mixture of oleic acid and phthalic anhydride. The primary function of oleic acid is to attract the magnesium oxide which reduces the activity of magnesium oxide with polyester, as shown in Fig. 2. Phthalic anhydride is used primarily to consume the water so as to reduce the hydrolysis ability of magnesium oxide in the initial thickening period and to avoid the suppression of the thickening reaction by excess water in the final thickening period. Also, after the phthalic anhydride is reacted with the water, phthalic acid is formed and is able to suppress the thickening reaction in the initial thickening period, as shown in Fig. 3 and Fig. 4.

Fig. 2 : Thickening effect of oleic acid measured by the resin base procedure

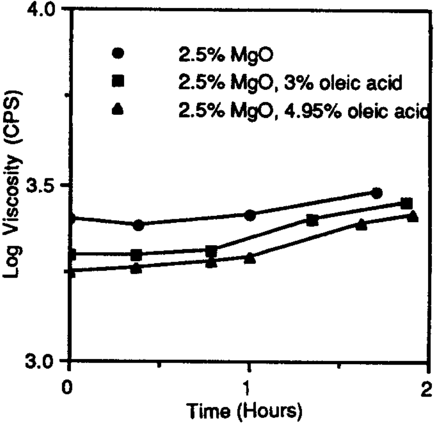


Fig. 3 : Thickening effect of phthalic anhydride measured by the resin base procedure (the initial thickening period)

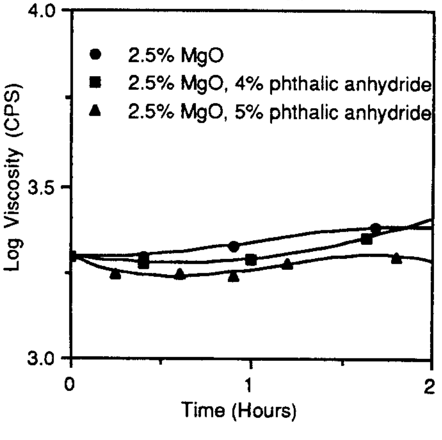
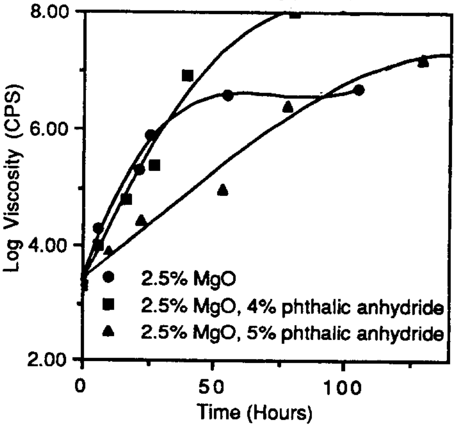


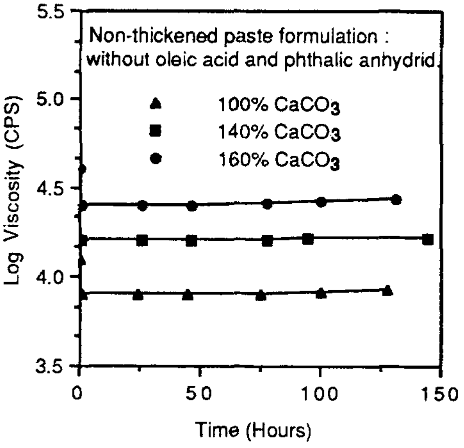
Fig. 4 : Thickening effect of phthalic anhydride measured by the resin base procedure (the final thickening period)



According to Horner et al., the desirable water content is in the range 0.05% - 0.15%(4). Under the wet climate condition of this experimental work, the water content trapped from the atmosphere was 0.27±0.08% in the paste and was a bit too high. Since the water content has such a significant influence on thickening behavior, phthalic anhydride was used to consume the excess water. However, too much phthalic anhydride could cause excess water consumption. In order to keep an appropriate amount of water content in the paste, oleic acid was added to reduce the initial thickening reaction and to prevent too much water from being consumed by the anhydride. Thus an appropriate ratio of oleic acid and phthalic anhydride is required to make a good thickening control agent. These data are shown in Table 1.

In view of equations (1-1), (1-2), and (1-3), it is found that calcium carbonate is likely to act as a thickener. But in Fig. 5, no obvious thickening behavior is observed without any thickener present in the paste. This indicates that calcium carbonate is not a thickener. By comparing the coefficients of calcium carbonate in the equations to those of the other components, it can be seen that calcium carbonate has a tremedous effect upon thickening curves. Therefore, this shows that calcium carbonate not only raises the viscosity level but also accelerates the thickening rate. There is also an upper threshold to the amount of calcium carbonate being added to the SMC paste. This follows the fact that too much calcium carbonate can result in too short an initial thickening period for the wetting process to meet the requirements of SMC operation.

Fig. 5 : Thickening effect of calcium carbonate measured by the paste base procedure



From equation (1-3), it is observed that magnesium oxide has the largest influence on the final average viscosity. This thickening behavior shows the viscosity increase results from the thickening reaction between magnesium oxide and polyester resin. This means that the final viscosity will not be raised high enough to reach the moldable region if the thickener present in the paste is not adequate.

Equations (2-2) and (2-3) refer to the effect of temperature on thickening curves. Temperature shows the most significant influence on thickening curves, even overwhelming that of the control agent. It is observed that after the initial thickening period, a temperature increase can drastically increase the thickening rate. By investigating all the above equations, it is found that the main effects, such as the thickener, the thickening control agent, calcium carbonate and temperature all play important parts upon thickening curves. Since the effects of the interactions are very small compared to the main effects, it is convenient and reasonable to discuss these main effects only and neglect the effects of interactions on thickening curves.

From the discussion above, it is obvious that magnesium oxide plays the main role in the thickening reaction. The thickening control agent can prolong the initial thickening period. Calcium carbonate shortens the time of the initial thickening period. Temperature increases the middle thickening rate and raises the final average viscosity.

An appropriate thickening curve could be obtained by optimizing the following parameters:

(1) the thickener which thickens the paste.

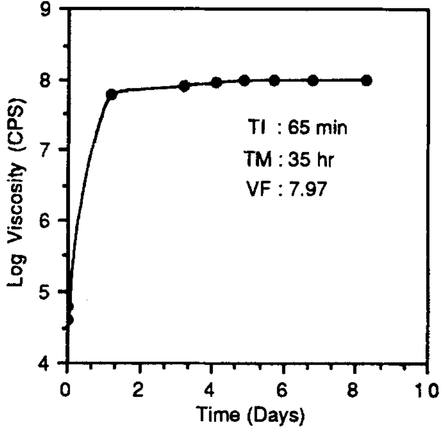
(2) the thickening control agent which prolongs the initial thickening period.

(3) the added amount of calcium carbonate has to be decided very carefully by taking the cost and performance of SMC into consideration. Adding more calcium carbonate reduces the cost but decreases the mechanical properties at the same time. Besides having an upper threshold, calcium carbonate also possesses a lower threshold for avoiding phase seperation during storage.

(4) the increase in temperature which increases the thickening rate of the middle thickening period and can overcome the water effect. However it is to be noted that temperature has an upper threshold near 45°C (5).

In this experimental case, in order to obtain a better thickening curve it is reasonable to choose a low level of magnesium oxide, high level of the thickening control agent, high level of calcium carbonate (for the purpose of reducing cost) and high level of temperature during the first day of operation. Under such conditions, the thickening curve shown in Fig. 6 was obtained, with a longer initial thickening period, a shorter middle thickening period, and a more stable final viscosity period in comporison to both the high and low content level formulations shown in Table 1.

Fig. 6 : The thickening curve - paste viscosity vs. time



CONCLUSIONS

This study demostrates the advantages of using factorial design for obtaining a better understanding of SMC thickening behavior and for obtaining an excellent thickening curve.

Within the limits of the experiments, one may conclude:

1. From the experimental results of factorial design, the thickening control agent helps to set up an appropriate thickening curve in two ways. First, oleic acid is used to reduce the thickening activity of magnesium oxide with polyester resin. Second, phthalic anhydride is used to overcome the water effect and reduce the thickening activity of magnesium oxide with polyester resin. The results also indicate that the mixture of oleic acid and phthalic anhydride has to be maintained at a proper ratio.
2. Calcium carbonate not only raises the viscosity level, but also acts as a thickening accelerator.
3. The thickener plays the main part in raising the viscosity.
4. Temperature has the most significant influence on thickening curves by promoting the thickening activity of magnesium oxide with polyester resin, greatly increases the middle thickening rate and the final average viscosity.

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