

CHAPTER III

RESULTS AND DISCUSSION

Unsaturated polyester resins must be formulated to a relatively low viscosity such as at about 1000 mPa-s or they must be able to reduce viscosity by additional styrene monomer. This is because of the need for easy flow through the reinforcing material at the time of molding. The amount of filler that can be used is also limited by the viscosity requirement, and the best function of filler must be the one that does not separate from the paste compounding when flows in the mold (8).

In addition, SMC compound must remain homogeneous when it flows through the mold. If the resin, filler or glass fiber separate, serious variations in properties will occur throughout the molding. The ideal compound should also flow easily and fill extremities of the mold (9). The resins usually vary in their ability to wet the fillers and reinforcing material, depending on their viscosity and basic chemical structure. For filler, the CaCO_3 must be well dispersed in the resin mixture (8). It is a good practice to blend initially the filler with as little resin as possible until the mix forms a homogeneous mixture.

The problem of formulating a compound that possesses satisfactory flow and maintains homogeneity, is the selection of type and the amount of the resin and filler combination. A high viscosity resin mix will carry reinforcing material and filler well, but it makes mixing difficult in the preparation of SMC sheet.

3.1 Effect of Filler and Thickener on Viscosity

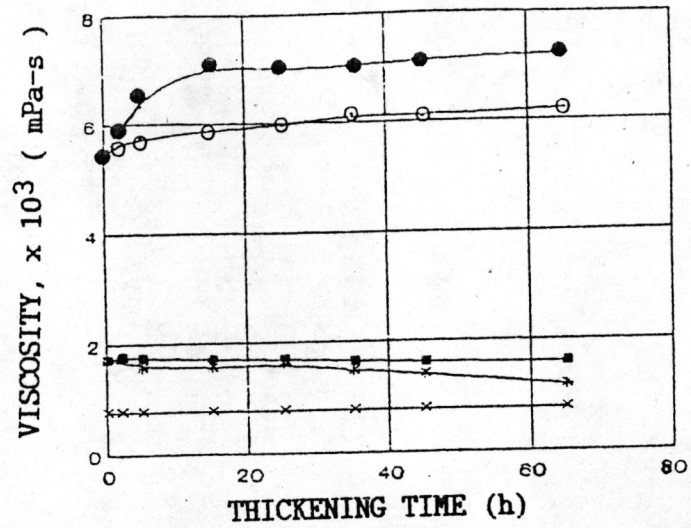
In the formulation of SMC which consists of resin, filler, reinforcing material, thickener, catalyst and mold release agent. Catalyst and mold release agent do not effect to the thickening behavior of polyester molding compound during the thickening period, because the amount of these ingredients present is relatively small compared to other ingredients and because they are commonly inactive while thickening reaction takes place. Therefore, selecting the compounding ingredients especially filler and thickener are crucial from which the effects of these materials on the thickening behavior of unsaturated polyester resin are investigated.

However, the present study did not focus on the mechanism of thickening behavior of compounding but their behaviors were used as a basic knowledge, in practice, to understand the preparation of sheet-form molding compound.

3.1.1 Effects of Filler on Viscosity

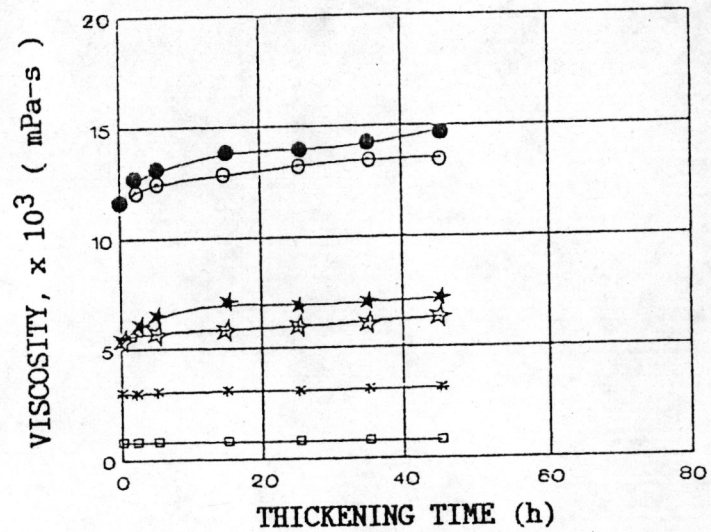
In order to investigate the effect of filler on the thickening behavior of polyester resin containing CaCO_3 particles, with and without surface treatment with organic acid (stearic acid), and both of them in the absence of the coupling agent, the experiments were carried out separately. It is seen in Figure 3.1, that the resin containing treated CaCO_3 particles has viscosities higher than the resin containing the untreated CaCO_3 . Since the coupling agent has, particularly, a long chain of stearic acid, $\text{CH}_3(\text{CH}_2)_{16} \text{COOH}$ or R-COOH when R is $\text{CH}_3(\text{CH}_2)_{16}$, the former might have dispersed well in the resin. This causes, the rise of viscosity compared to the untreated system. The untreated system gives a decrease in viscosity because CaCO_3 might not be able to form particulate with the resin but it can precipitate in the resin. It is obviously to see the clarity in the resin mix and simultaneously coagulated CaCO_3 particles at the bottom of glass container.

When the treated CaCO_3 particles were added to the resin, the viscosity of the mixture increases accordingly with the relative amount of filler. Figure 3.2 shows the result of the viscosity due to the effect of CaCO_3 loading. However, as shearing forces and temperature increased, the particles which dispersed in the resin containing the surface treated CaCO_3 began to break down, yielding lower viscosity. In addition, two particle sizes of CaCO_3 were used, 3.0 and 6.5 micrometer average



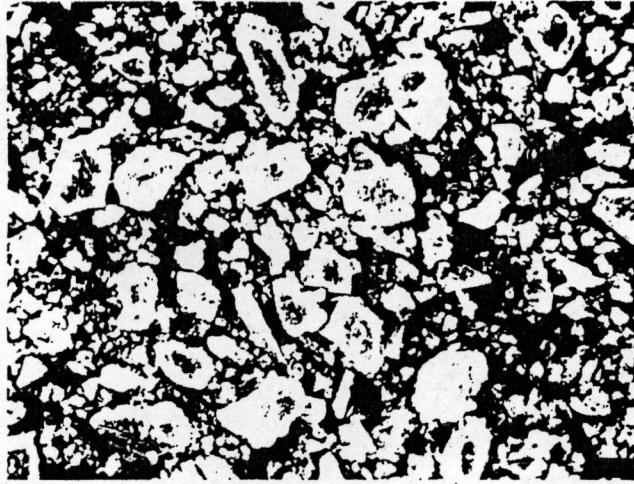
- 28°C, treated CaCO₃
- 36°C, treated CaCO₃
- 28°C, untreated CaCO₃
- * 36°C, untreated CaCO₃
- × pure resin

Figure 3.1 Effect of thickening time of treated and untreated CaCO₃ filler in the resin on viscosity.



- 120% CaCO₃, 36°C
- 120% CaCO₃, 28°C
- * 40% CaCO₃, 28°C
- ☆ 80% CaCO₃, 36°C
- ★ 80% CaCO₃, 28°C
- 0% CaCO₃, (pure resin)

Figure 3.2 Effect of thickening time of the resin at various filler loadings on viscosity.



(a)



(b)

Figure 3.3 Electron micrographs (magnification 2000 x) show the morphology of:

- (a) the crystal of CaCO_3 particles
- (b) the wetting of treated CaCO_3 particles with resin matrix

diameter. The system containing the CaCO_3 of small particle size, gave higher viscosities than those of the system containing the large particle size (11). This behavior was expected because the smaller particles had more surface area available to interact with the resin than the same weight of larger particles.

As the viscous behavior of resin- CaCO_3 system presented above, may be increased or decreased by such treatment. The adhesion between the matrix and particles was induced by the treated filler. In Figure 3.3(a)-(b) an example of the morphology of a cross-sectional surface area shows wetting of the treated CaCO_3 particles in the system. It depicts the existence of homogeneity of the matrices and illustrates possibly the high viscosity of the system when the treated CaCO_3 is mixed with the resin.

3.1.2 Effect of Thickener on Viscosity

In order to make SMC suitable for molding operation, the viscosity of the compounds is made up to increase more than 10^6 mPa-s. It has been suggested in the literature (16) that the thickening behavior is a result of chain extension brought about by the condensation reaction between the Group IIA metal oxides and the carboxylic acid groups present in the unsaturated polyester resins. Among Group IIA metal oxides and/or hydroxides used as thickeners, magnesium oxide (MgO) is a popular choice because of its high reactivity and

the low concentration required for thickening behavior. The effect of MgO in inducing a workable thickening condition in SMC has not as yet clearly understood. What is understood is the visible physical changes that occur to form an improved molding compound. The viscosity changes are measurable by viscometer which is set up on a time schedule through the course of mixing.

The viscosity of polyester molding compounds is determined by the level of chemical thickener in the resin mix, which influences the molding characteristics. Since the higher the viscosity, the higher the molding pressure required. At some point, completely fill out of the mold may become a problem, and the product is usually rejected. On the other hand, too low a viscosity can cause the resin to flow ahead of the glass fiber and results in resin-rich areas with low mechanical properties.

Two sets of experiments were set up to determine the thickening behavior of the unsaturated polyester resin inclusive of the thickener only, without any fillers. Their behaviors were studied in three concentrations of MgO at two different temperatures. Figure 3.4 depicts the relationship between the thickening time and viscosity. It was seen that the viscosity of resin increased very rapidly and tended to go through a maximum as the thickening time progressed. At high maturation temperature of 36°C, the viscosity increased more rapidly than that at low temperature (room temperature, 28°C).

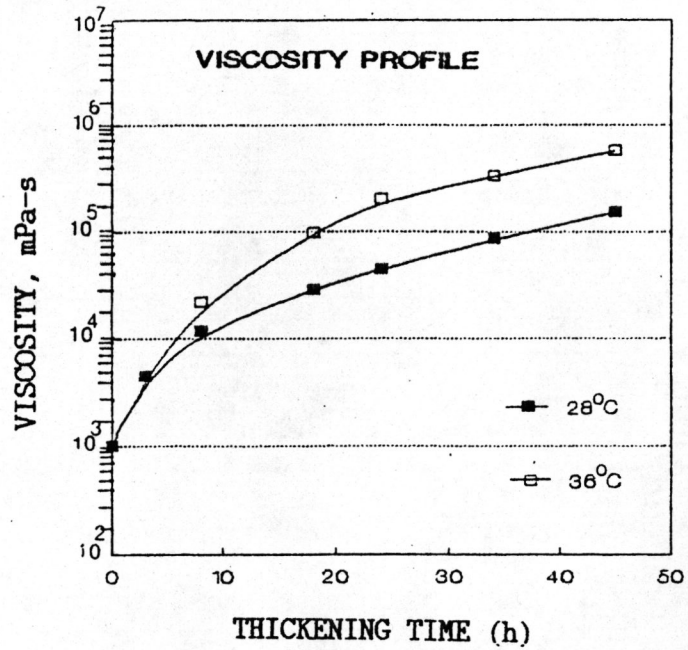


Figure 3.4 Effect of thickening time, for the viscosity of resin in the presence of 3 % MgO at 28°C and 36°C.

Table 3.1 The viscosity of resin mix changes with the time at the different concentrations of MgO.

Time, t (h)	Rate of change of viscosity, dn/dt (mPa-s/h)		
	3% MgO	5% MgO	7% MgO
2	1,175	4,815	14,057
5	3,376	16,816	29,990
13	7,390	22,400	31,400
20	17,315	23,500	69,830
30	12,880	27,500	77,330
40	26,775	60,725	98,910

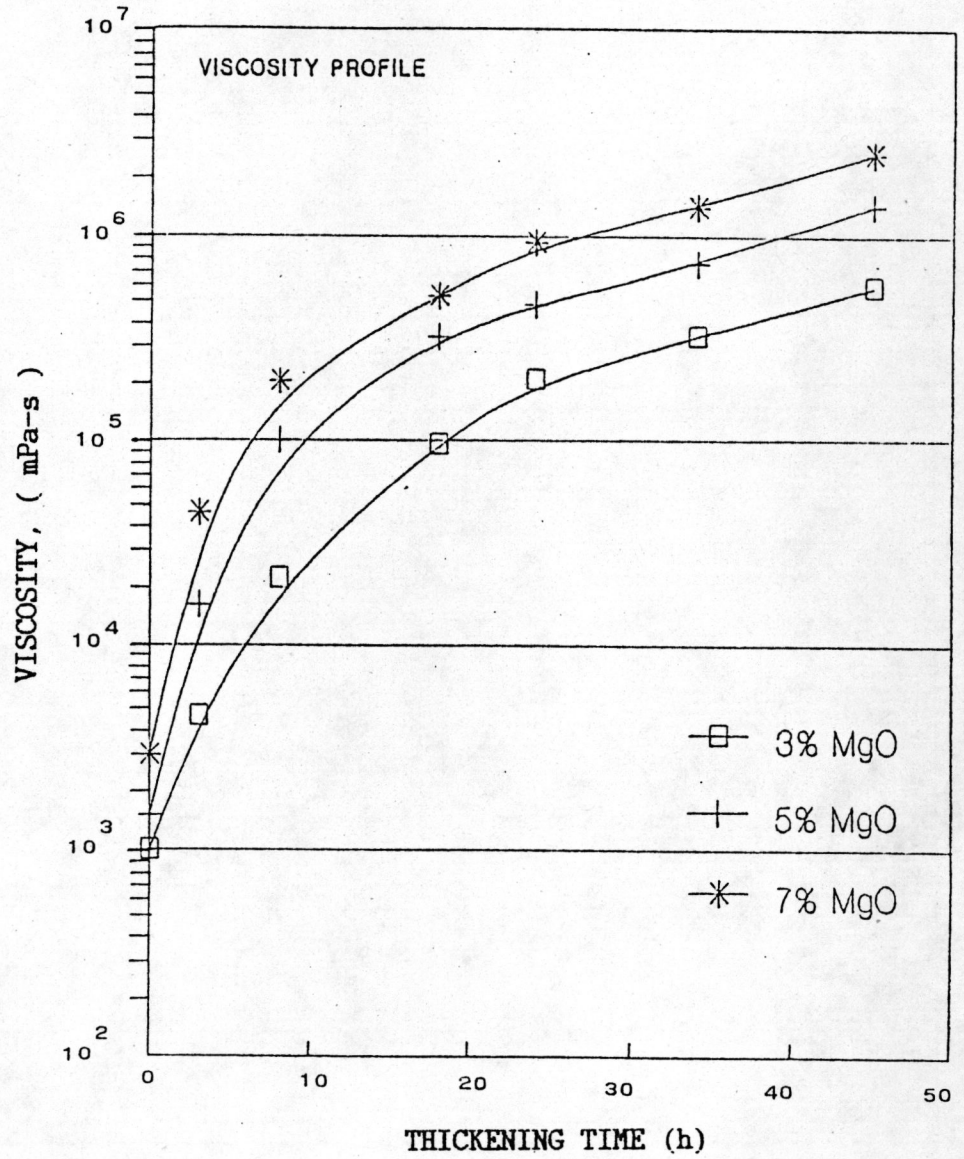
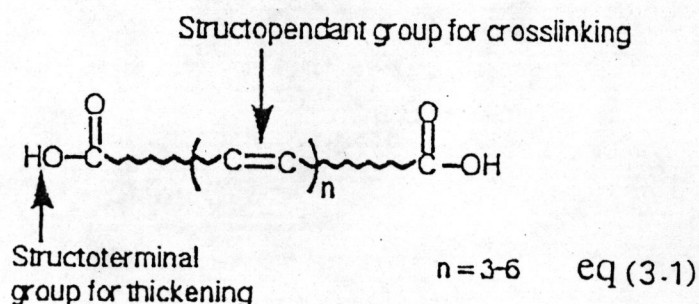


Figure 3. 5 Effect of the % MgO in term of thickening time on viscosity at 36°C.

It was noted that the viscosity of the control sample (ie, without MgO) remained constant over the period of thickening time. The viscosities are illustrated in Figure 3.5, and Table 3.1 showed the rate of changes of the viscosity at the different concentrations of MgO. One can obtain that the viscosity increases with increasing the concentrations of MgO.

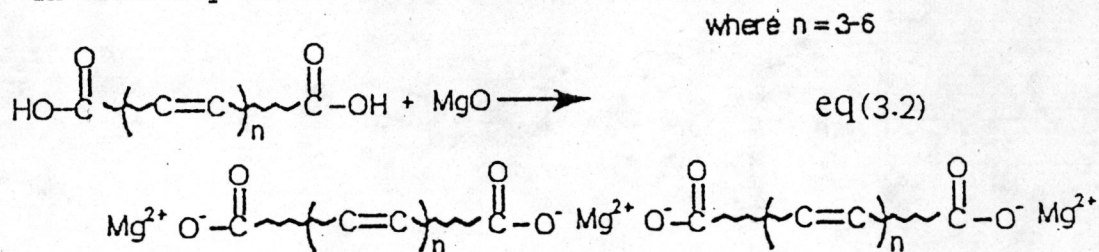
In these results, an excessive increase in the viscosity of polyester resin takes place by its modification with MgO. However, the chemical background of this process has not been clarified. As illustrated in equation 3.1, the general purpose unsaturated polyester resin contains structopendant reactive groups for crosslinking and structoterminal reactive groups for thickening reaction (16).



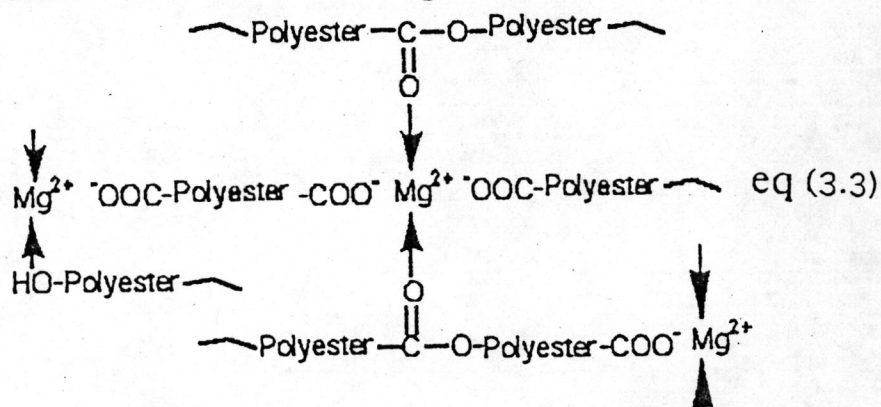
The molecular structure of the unsaturated polyester resin (equation 3.1), would be expected to have an effect on the rheological properties of the molding compounds during thickening period or cure. The reaction of MgO with polyester resin containing the carboxyl end groups may lead to

compounds with very high viscosities and it is referred to as the thickening reaction of polyester resin. The exact mechanism of thickening reaction is not well understood. Several other investigators have proposed different mechanisms for this complicated reaction. More details of these different mechanisms were described in APPENDIX C.

The following two reaction mechanisms had been extensively studied by some authors (16, 17, 18). Starting from the formation of basic or neutral magnesium carboxylates. The formation of linear ionic macromolecules by coupling of magnesium carboxylate chain ends could account for the observed increase in viscosity which has illustrated in equation 3.2 (16).



A two-step reaction between the carboxyl end groups and MgO, with initial formation of basic or neutral salts was involved, and followed by the coordination complex of these salts between the ester groups and Mg^{2+} ions, leading to a network structure as illustrated in equation 3.3 (17).



In view of the CaCO_3 filled unsaturated polyester, the fact that CaCO_3 cannot be dissolved in polyester resin, the behavior observed as the level of viscosity has been shown in Figure 3.2. It can then be concluded that the CaCO_3 seems to have little influence on the thickening effect of the resin mix systems. Whenever the MgO added can dissolve in styrene monomer and can react with unsaturated polyester which leads to high viscosity and then increasing up to a jelly-like mass.

3.1.3 Effect of the Combined Addition of Filler and Thickener on Viscosity

Having described the effects of filler and thickener separately on the thickening behavior, then the experiments proceeded to study the effects of these two ingredients when added together as shown in Figure 3.6. The viscosity variations when CaCO_3 alone and MgO alone was added to the polyester resin were also relatively illustrated.

In addition, Figure 3.7 illustrates the combined effect of filler and MgO , on viscosity in term of thickening time of the unsaturated polyester resin. It is seen that the viscosity is progressed. Comparison of each viscosity curve in Figure 3.7, one observes that the magnitude of viscosity of the resin-thickener-filler system. In other words, during the thickening period the CaCO_3 enhances the thickening effects of the mixtures of polyester resin and thickener. Rate of changes

on the viscosity in the presence of 3% MgO at the difference concentrations of CaCO_3 , was shown in table 3.2. The rapidly increase in viscosity observed, the CaCO_3 in the resin-thickener system may be attributable to the formation of the particulate phase that has resulted from the presence of CaCO_3 particle. Undoubtedly, the state of dispersion is very complex, however, the net effect is to bring about the gross increase in viscosity of the system.

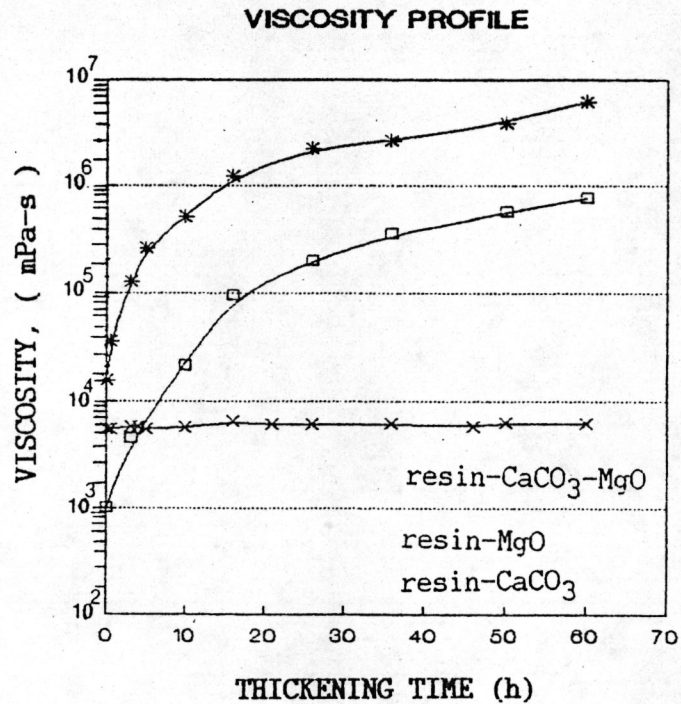


Figure 3.6 Effects of CaCO_3 and MgO on the thickening time and viscosity.

Additionally, the thickening effect also depends on both time and temperature at which thickening reaction takes place over the entire period of reaction. At the maturation temperature about 36°C , the thickening effect can be

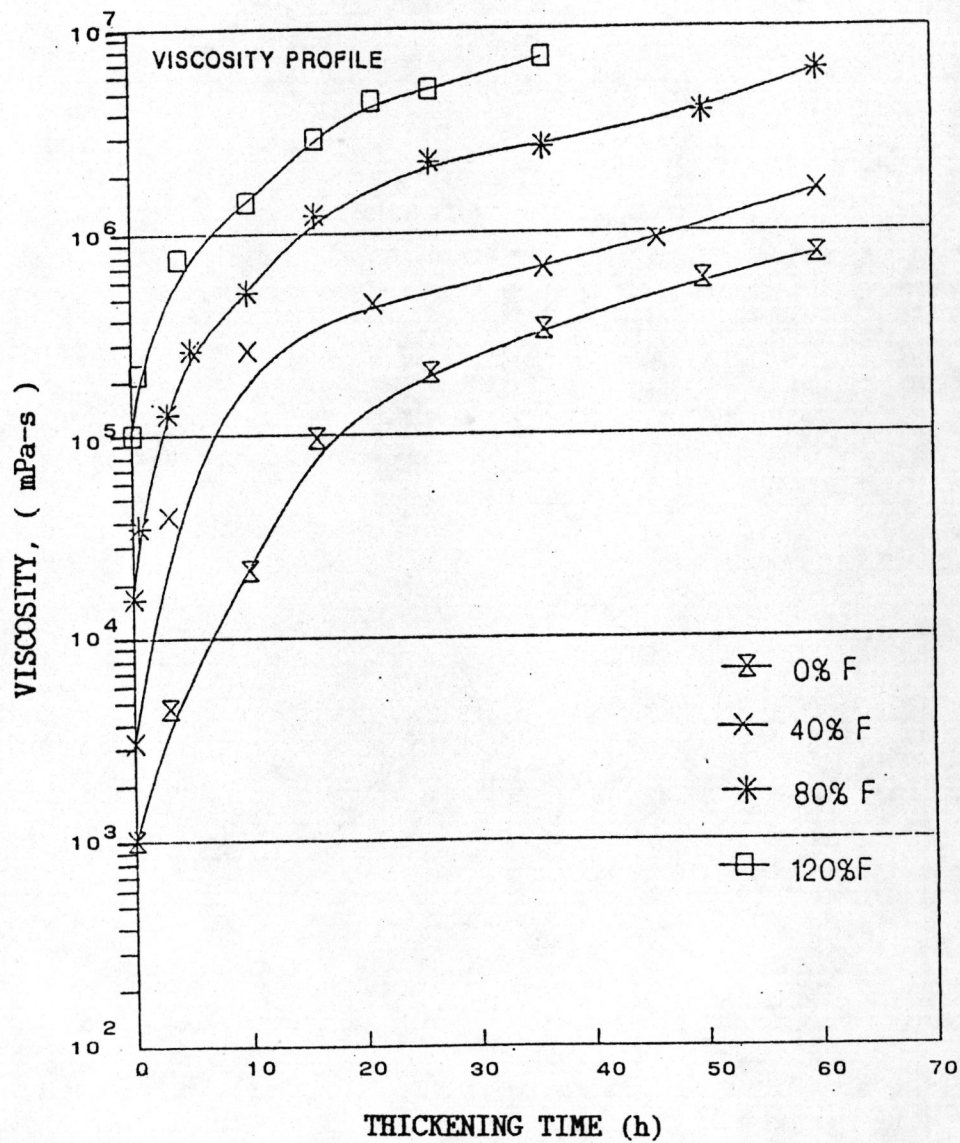


Figure 3.7 Comparison of the combined effect of CaCO_3 and MgO on viscosity.

Table 3.2 The viscosity of resin mix changes with the time at the different concentration of CaCO_3 in the presence of 3% MgO .

Time, t (h)	Rate of change of viscosity, $d\eta/dt$ (mPa-s/h)			
	0% CaCO_3	40% CaCO_3	80% CaCO_3	120% CaCO_3
2	1,175	12,261	37,070	161,400
5	3,376	31,620	54,874	113,330
13	7,390	12,449	65,545	249,330
20	17,315	11,400	100,010	213,600
30	12,880	18,200	93,866	224,800
40	26,775	-	87,715	-

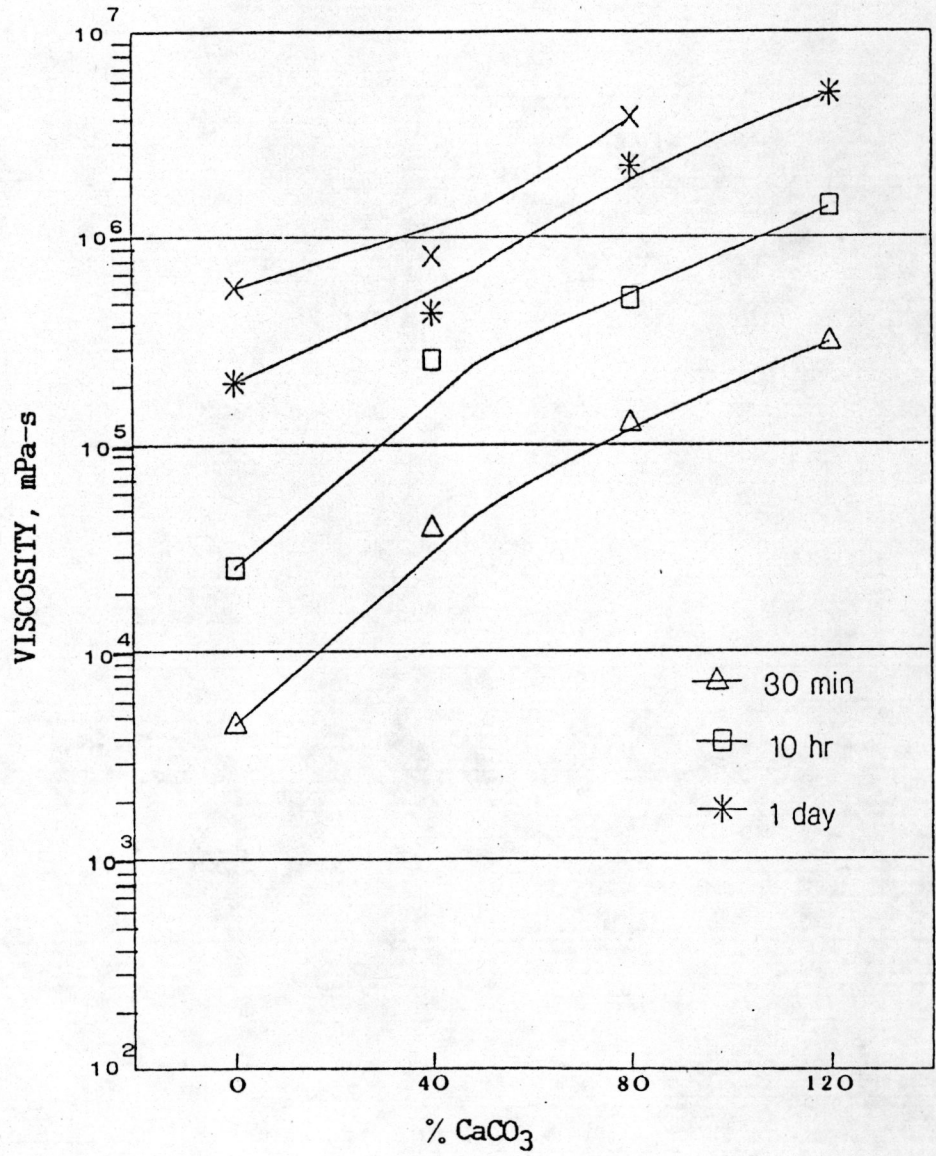


Figure 3.8 Effect of the concentrations of CaCO₃ in the presence of 3 % MgO, at different times on viscosity.

formed quicker than that at room temperature (about 28°C). Apart from the thickening effect of the filler in the presence of thickener, the system does not only depend on temperature but also depend on the time progress as shown very clearly in Figure 3.8.

3.2 Effect of Thickening Behavior on Maturation and Storage Life

From the previous discussions of thickening behavior, viscosity is determined at different times for the development of a thickening profile of the viscous resin. Determination of the viscosity at the end of the 1-2 hours (at 36° C), is to measure how rapid the SMC can be expected to thicken. The developments of maturation points on the viscosity profile have an optional time schedule. The profile of maturation rate is usually determined at the end of 24 hours (14). It may be plotted as increment of every 10 hours just like in this experiment, until the matured sheet reaches the proper molding viscosity. Maturation or aging suitable for molding may take 5 to 10 days at room temperature, but it will take 2 to 3 days at 36° C. At this time it is expected that the thickened material has a high viscosity to molding process.

Besides maturation, thickening of the SMC sheet also continues during storage. The points on the curves (which have been shown in Figures 3.3-3.8) are designated for projection of

STORAGE LIFE OF SMC

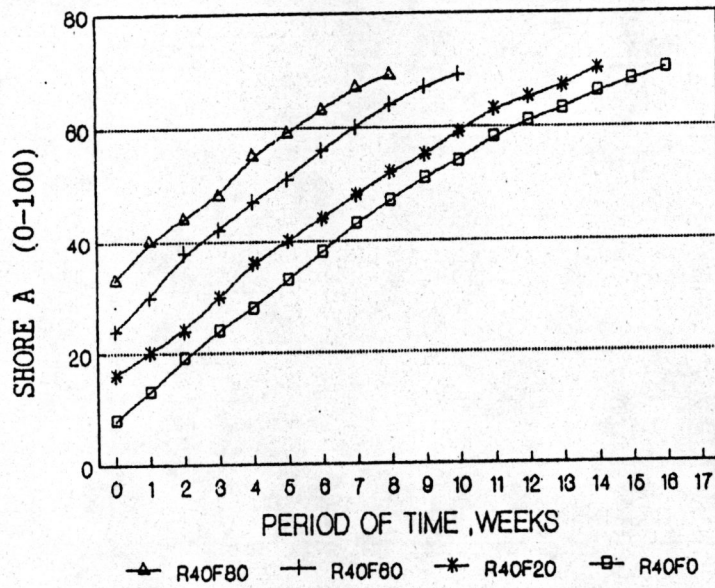


Figure 3.9 Effect of time on hardness of the SMC in the presence of various concentrations of glass fiber and CaCO_3

STORAGE LIFE OF SMC

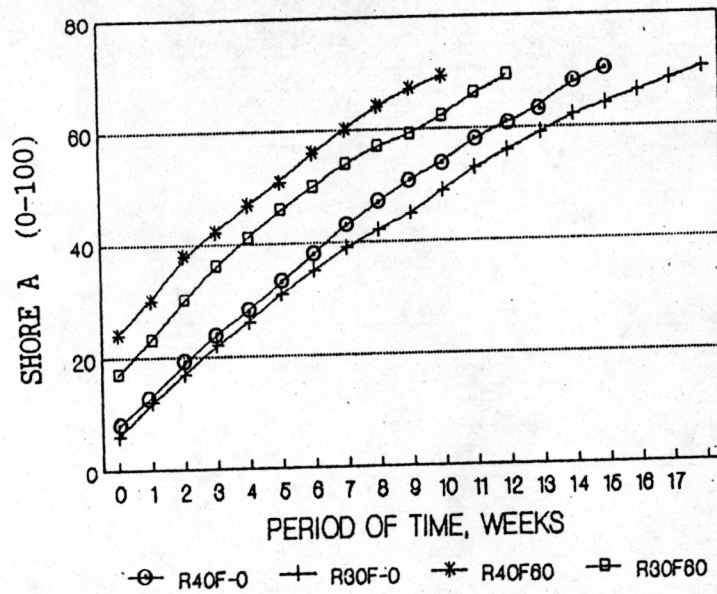


Figure 3.10 Effect of time on hardness of the SMC, without and with 60% CaCO_3 .
(R : Glass fiber and F : CaCO_3)

the time required for a sheet to reach the best part of the molding rheological characteristics. That is the point with a magnitude of a few million millipascal-second (mPa-s) to several million mPa-s. In general its viscosity may reach 10 to 60 million mPa-s after the maturation. These can be measured successfully by the Brookfield HBT viscometer equipped with the T-bar spindles. Unfortunately, its accessories are not available in this laboratory. However, due to the availability of such an instrument, type A of Shore Durometer is an optional instrument used in the experiments to determine the maturation period and the storage life of SMC. The method of testing conforms to ASTM D2240 (19). However, this method is not the best solution to determine the storage life of the SMC. Nevertheless, it can be used as a guideline to predict the storage life of this material.

From Figures 3.9 and 3.10, various compositions of SMC have different storage lives when kept at room temperature. The storage life of the SMC decreases with increasing in CaCO_3 filler and glass reinforcement in compounding. The experimental results showed that the storage life of the SMC at room temperature (28 C) could be as long as 2 months.

Because of the longer the storage time, the higher viscosity; the SMC sheet, then, becomes too hard to be indented on the surface. By the penetrating of the needle which is attached to Shore Durometer, the reading of the scale indicates

hardness of the SMC sample. By collecting the data from the durometer at set intervals, the thickening characteristics is determined and the storage life of SMC can be estimated. According to the experimental data, it is recommended that the SMC sample should not be denser than 60 scales of Shore A Durometer. If the SMC sample was indented and the scale reading process over 60, it indicated that the SMC was too dense to flow in the molding process.. It results in a hard compact and dense molded structure.

3.3 Effect of Reinforcing Material and Filler on Mechanical Properties

Mechanical properties of SMC depend primarily on the type of fibers, their quantity, and their direction. In SMC process, short fibers sometimes, referred to as chopped fibers, may be converted to a lightly bonded preform or mat that can be later impregnated with resin to fabricate single-layer composites. In this process, the chopped fibers are randomly oriented in planes parallel to the surface of the mold. Therefore, the properties of a chopped fiber reinforced composite can be isotropic; that is, the properties do not change with direction within the plane of the sheet. When the chopped fibers are blended with resins to make a sheet molding compound, these fibers tend to become oriented parallel to the direction of material flow during a compression molding operation and thus get a preferential

orientation the SMC which are the composites fabricated in this manner are anisotropic directions. Their properties depend on other things such as on the degree of preferential orientation achieved during the fabrication process.

The two outstanding features of oriented fibrous composites are their high strength : weight ratio and controlled anisotropy, it means that the desired ratio of property values in different directions can be easily varied(21). These two features make the fibrous composites very attractive structural composite materials. For structural SMC, this attention had been studied by Ralph B. Jutte (20); he developed versatile family of structural SMC and his results were summarized and referenced in APPENDIX F of this thesis. Because of the heterogeneous nature of SMC, they are conveniently studied from two points of view : micromechanics and macromechanics;

Micromechanics is the study of composite material behavior wherein the interaction of the constituent materials is examined on a microscopic scale.

Macromechanics is the study of composite material behavior wherein the material is presumed homogeneous and the effects of the constituent materials are detected only as averaged apparent properties of the composite (21).

In this thesis, the attention will first be focused on macromechanics. Subsequently, micromechanics will be investigated in order to gain an appreciation for how the constituents of SMC can be proportioned and arranged to achieve certain specified strengths and moduli.

3.3.1 Factors Influence Mechanical Properties of SMC: Macromechanics

In order to determine the strength and endurance of a material under stress, it is necessary to characterize its mechanical behavior. Moduli, strain, strength and toughness are measured macroscopically. These parameters are useful for materials selection and design.

Methodical testing procedures are an essential supporting knowledge for the utilization and improvement of fiber reinforced SMC composites. Standard tests that proposed by the ASTM, were selected in testing to be compared with similar testing by other investigators. A brief of mechanical test method is presented in APPENDIX C of this thesis.

The result of the ultimate strength for the SMC sample was plotted in tensile strength as a function of glass fiber content in Figure 3.11. Determination of the effect of glass fiber content to SMC sample on the flexural strength was shown in Figure 3.12, and for the impact strength was shown in Figure 3.13. The relationship of these curves (Figure 3.11 for tensile strength, Figure 3.12 for flexural strength and Figure 3.13 for impact strength) show that the glass fiber content affects the strength of SMC properties in a very direct manner. Any reduction in glass fiber content will result in the lowering of the SMC strength.

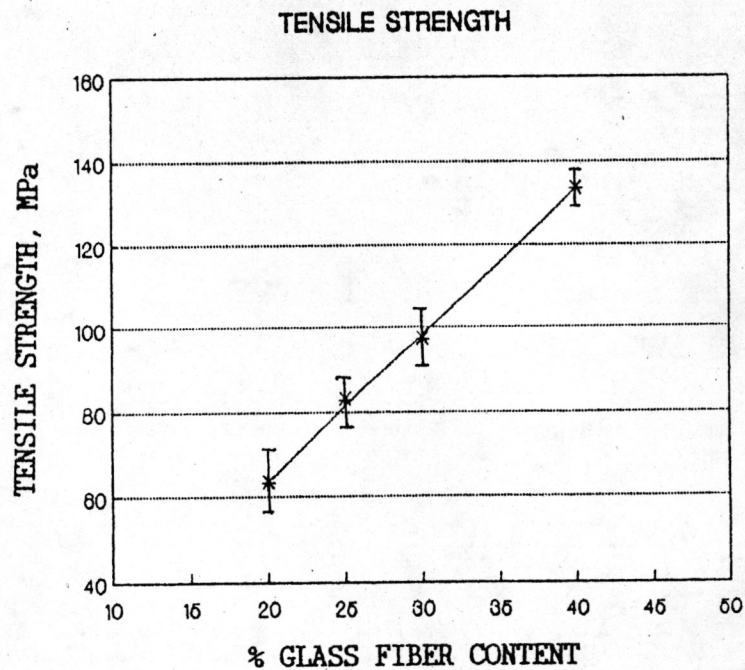


Figure 3.11 Dependence of tensile strength on % glass fiber content in SMC.

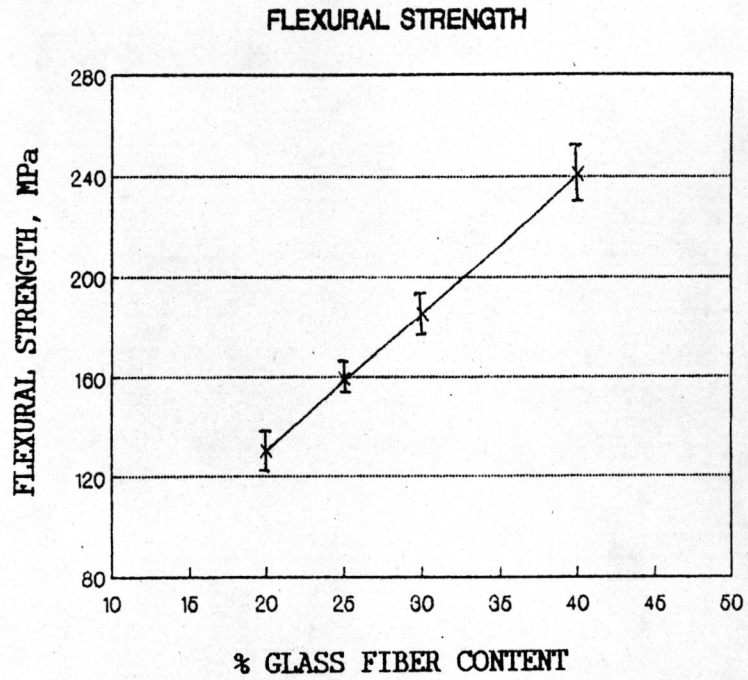


Figure 3.12 Dependence of flexural strength on % glass fiber content (without CaCO_3) in SMC.

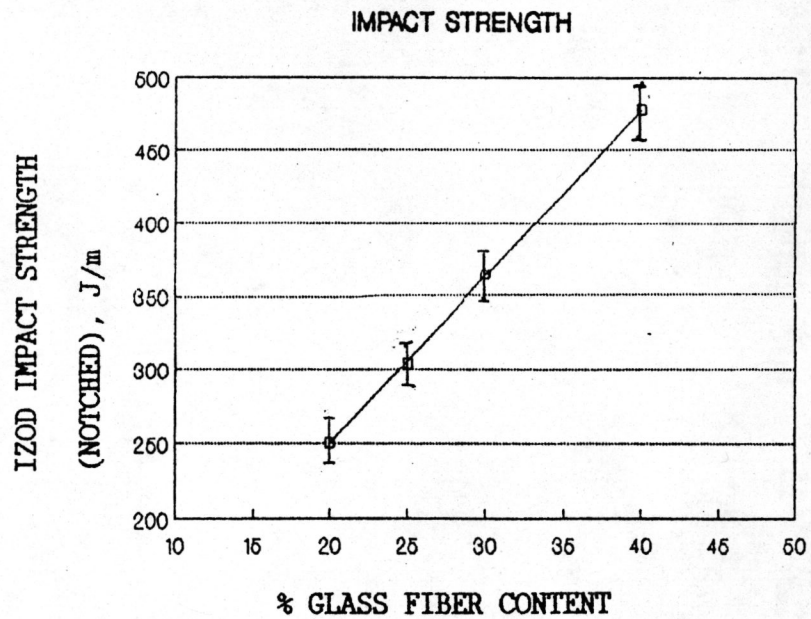


Figure 3.13 Dependence of Izod impact strength (notched) on % glass fiber content in SMC.

Figures 3.14 through 3.16 present tensile, flexural, and impact strength properties from a variety of compositions by varying the glass fiber contents and in the presence of varying the CaCO_3 contents for the polyester resin based on SMC systems. These Figures are based on data from SMC compound made with a variety of formulations that contained 20 to 40% glass fiber by weight of final compositions and 20 to 80% CaCO_3 by weight of resin. These properties generally vary linearly with glass fiber and CaCO_3 contents. The glass fiber contents have contributed more profound effect on strength rather than do the CaCO_3 contents to the SMC products.

In addition, the tensile and flexural moduli, as illustrated in Figures 3.17-3.18, increased with increasing the glass fiber and CaCO_3 contents simultaneously. The mechanical properties depend on formulation, especially glass fiber content and CaCO_3 content (Table 3.3). However, there are available data to compare the tensile moduli between the results from the experiments and the calculations from equation 5, derived and shown in APPENDIX E. Results of tensile moduli between the experimental and calculations for the different values of β , which is the co-factor of the fiber characteristics in this calculation, are illustrated in Figure 3.19. As shown, the experimental result has the same slope of the line of which β equals 0.375.

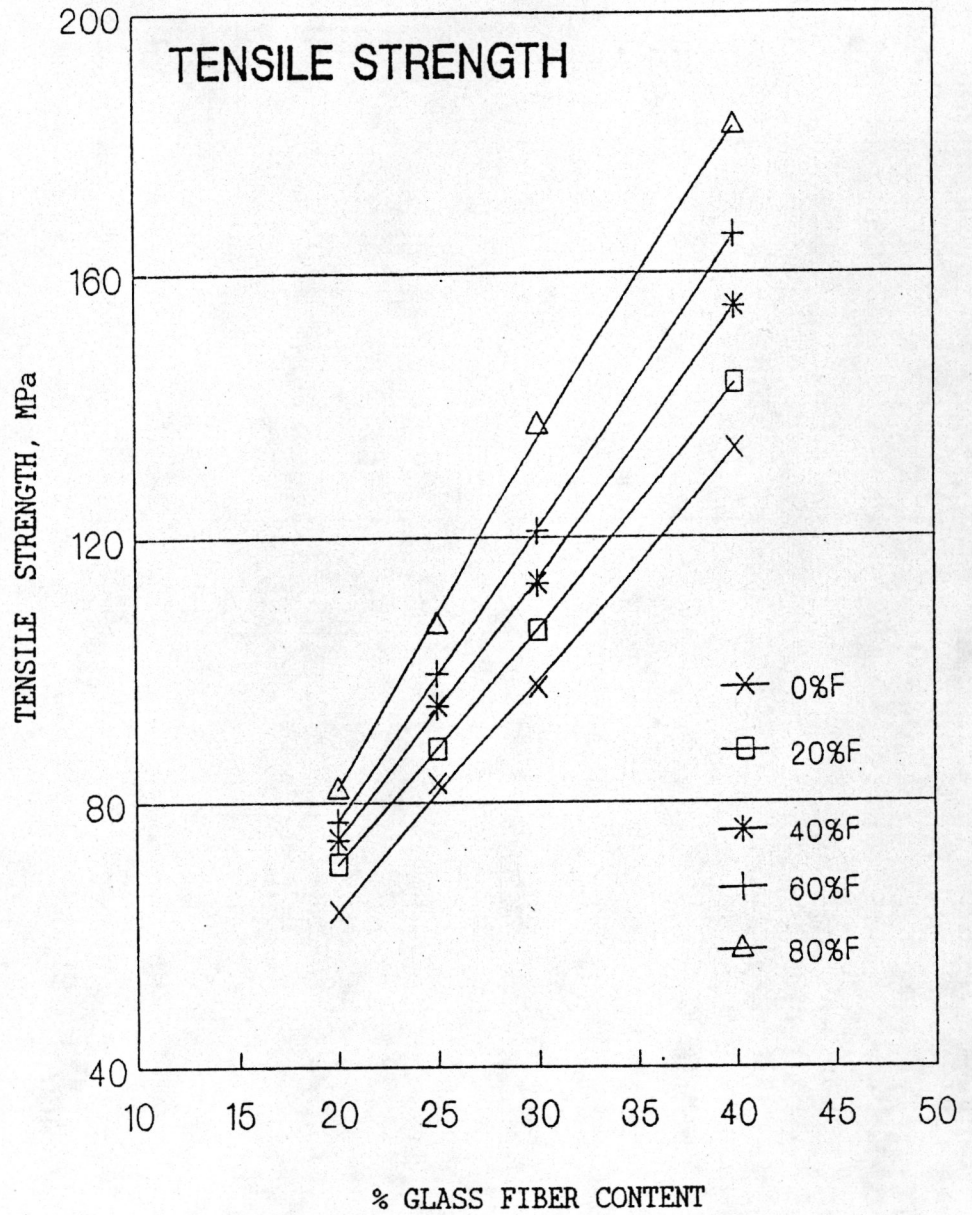


Figure 3.14 Dependence of tensile strength on % glass fiber content in the presence of different CaCO_3 contents.

(R : glass fiber and F : CaCO_3)

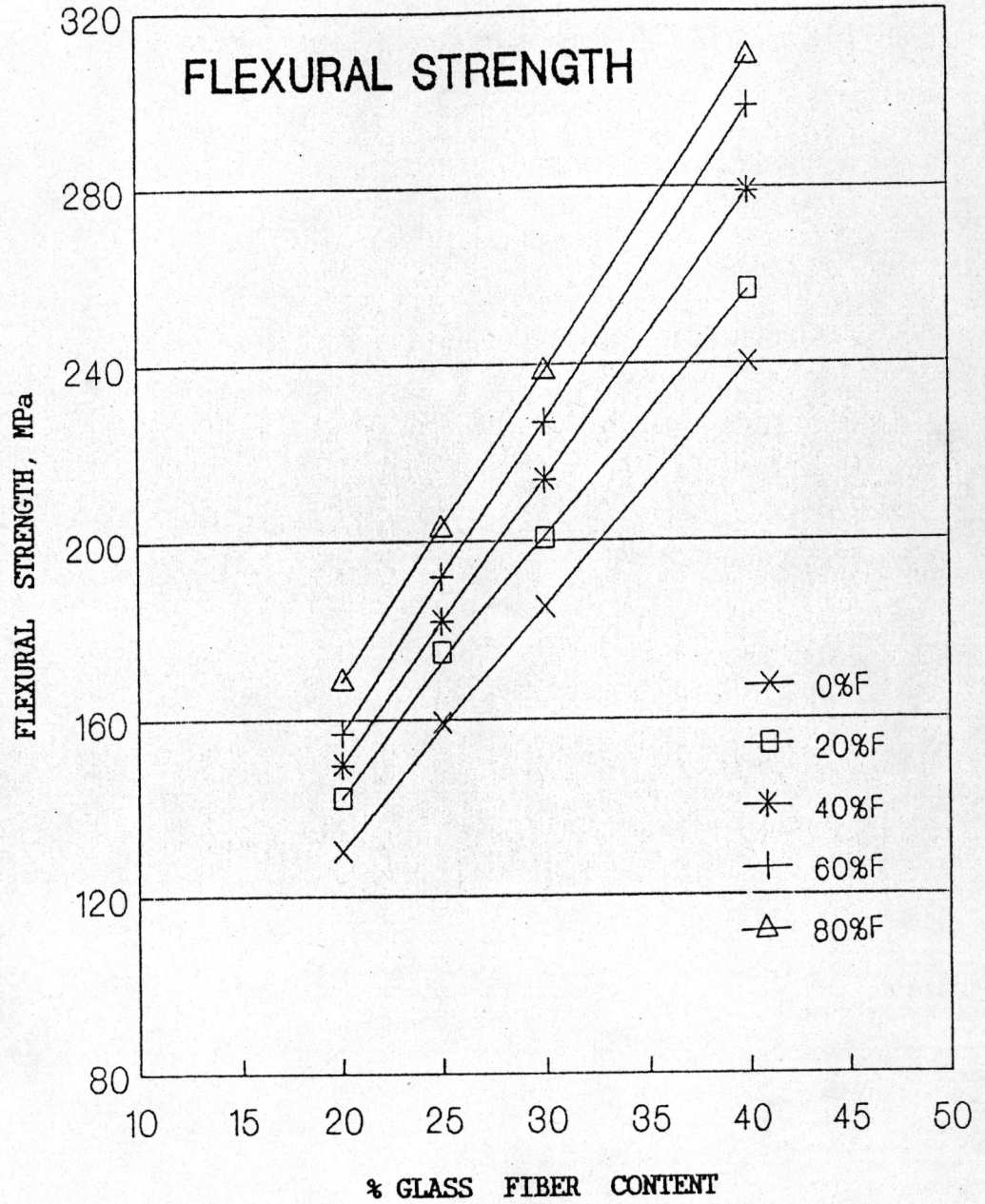


Figure 3.15 Dependence of flexural strength on % glass fiber content in the presence of different CaCO_3 contents.

(R : glass fiber and F : CaCO_3)

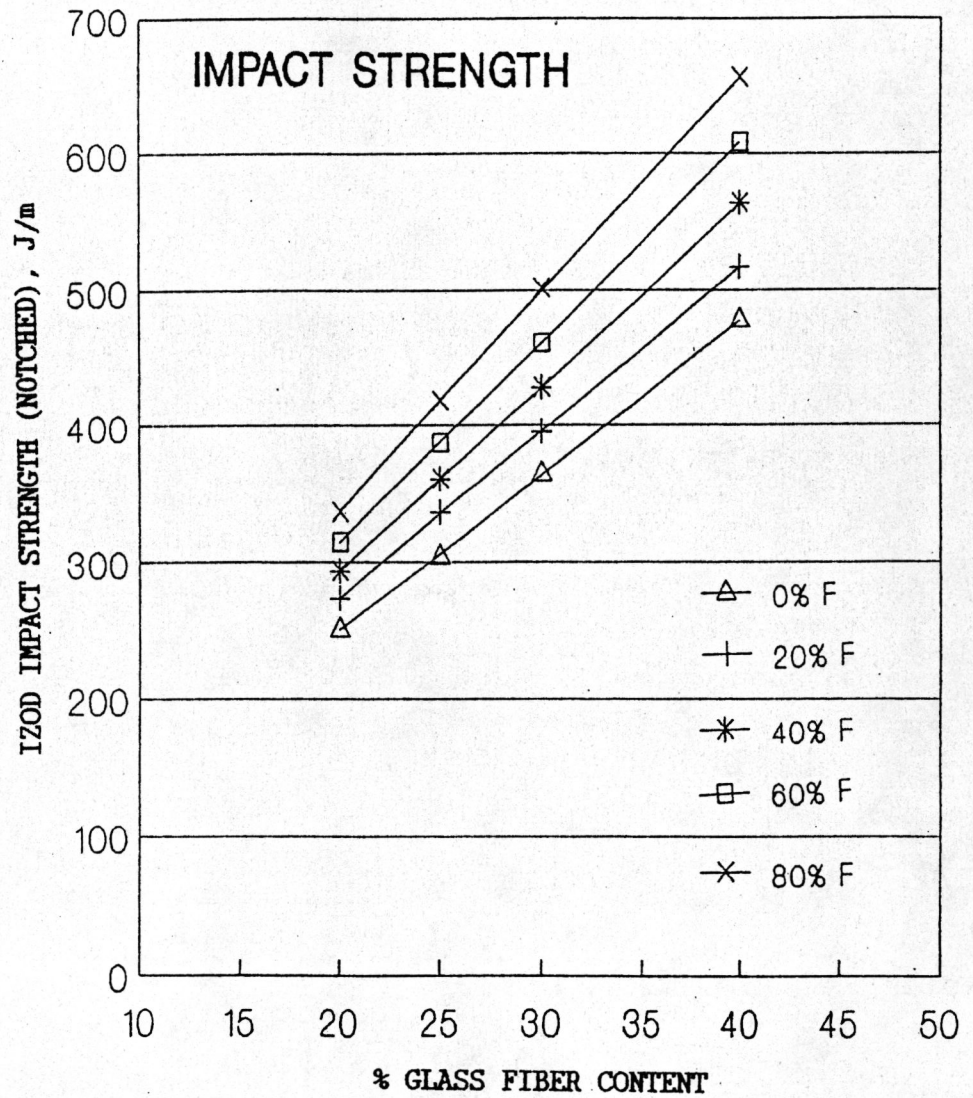


Figure 3.16 Dependence of Izod impact strength (notched) on % glass fiber content in the presence of different CaCO_3 contents. (R : glass fiber and F : CaCO_3)

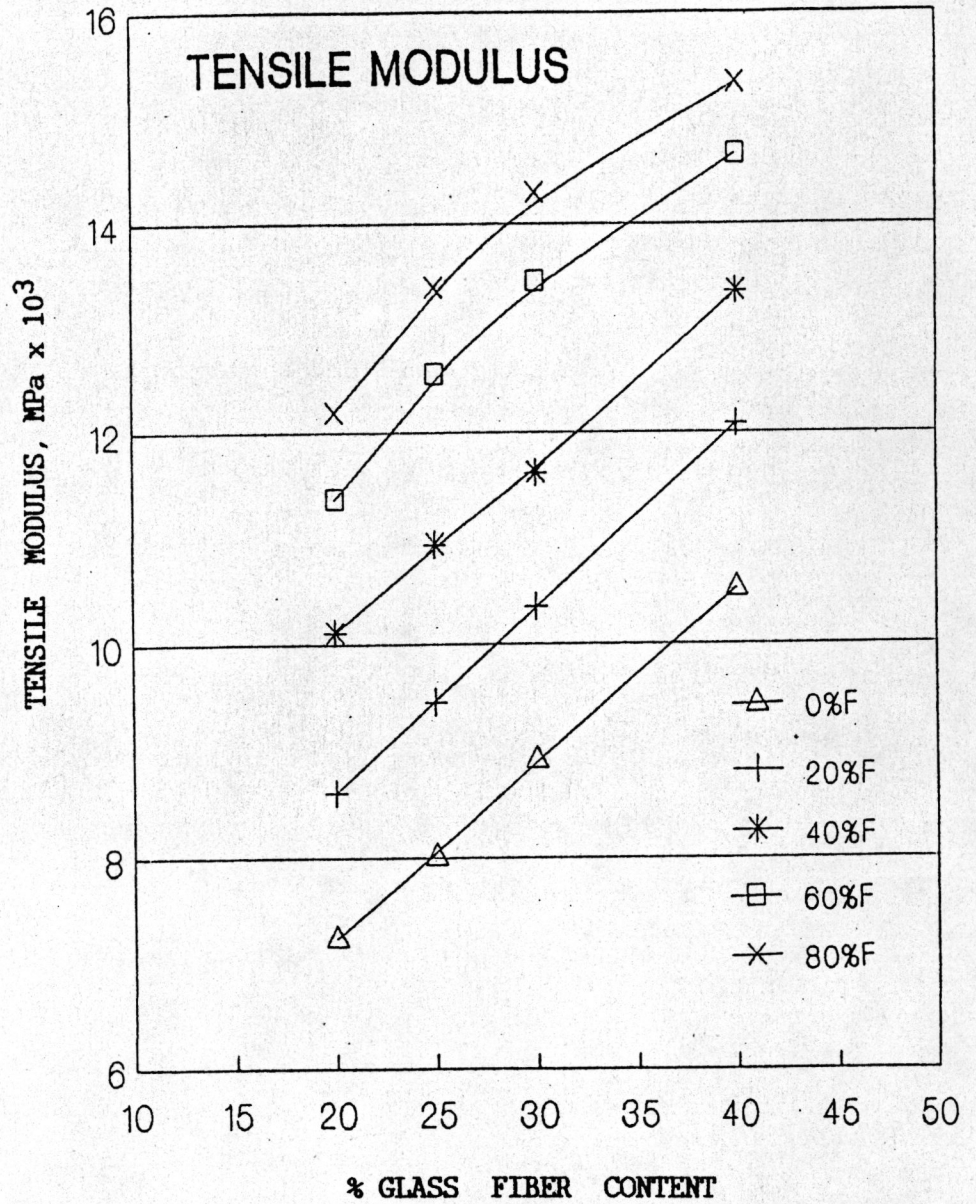


Figure 3.17 Dependence of tensile modulus on % glass fiber content in the presence of different CaCO₃ contents.

(R : glass fiber and F : CaCO₃)

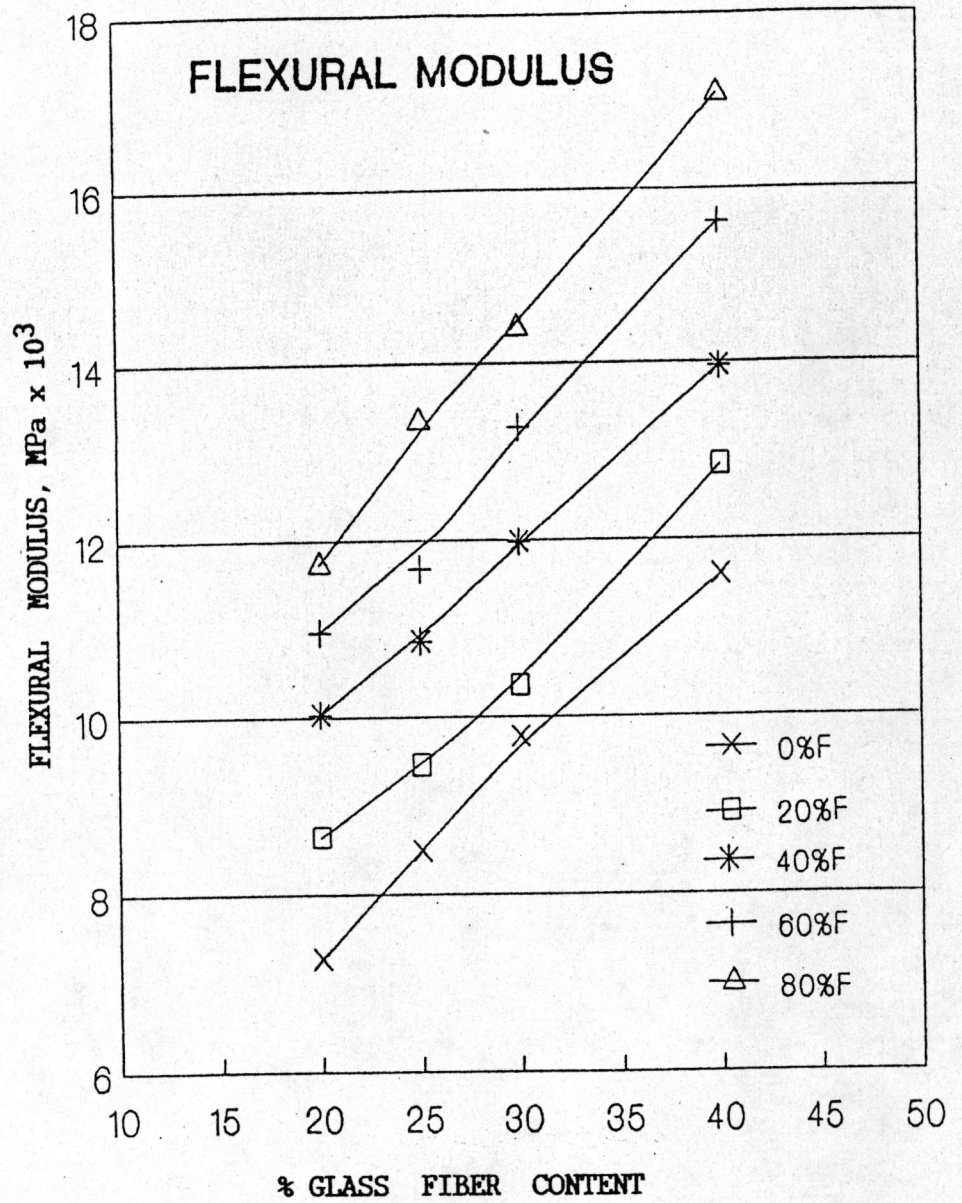


Figure 3.18 Dependence of flexural modulus on % glass fiber content in the presence of different CaCO₃ contents.

(R : glass fiber and F : CaCO₃)

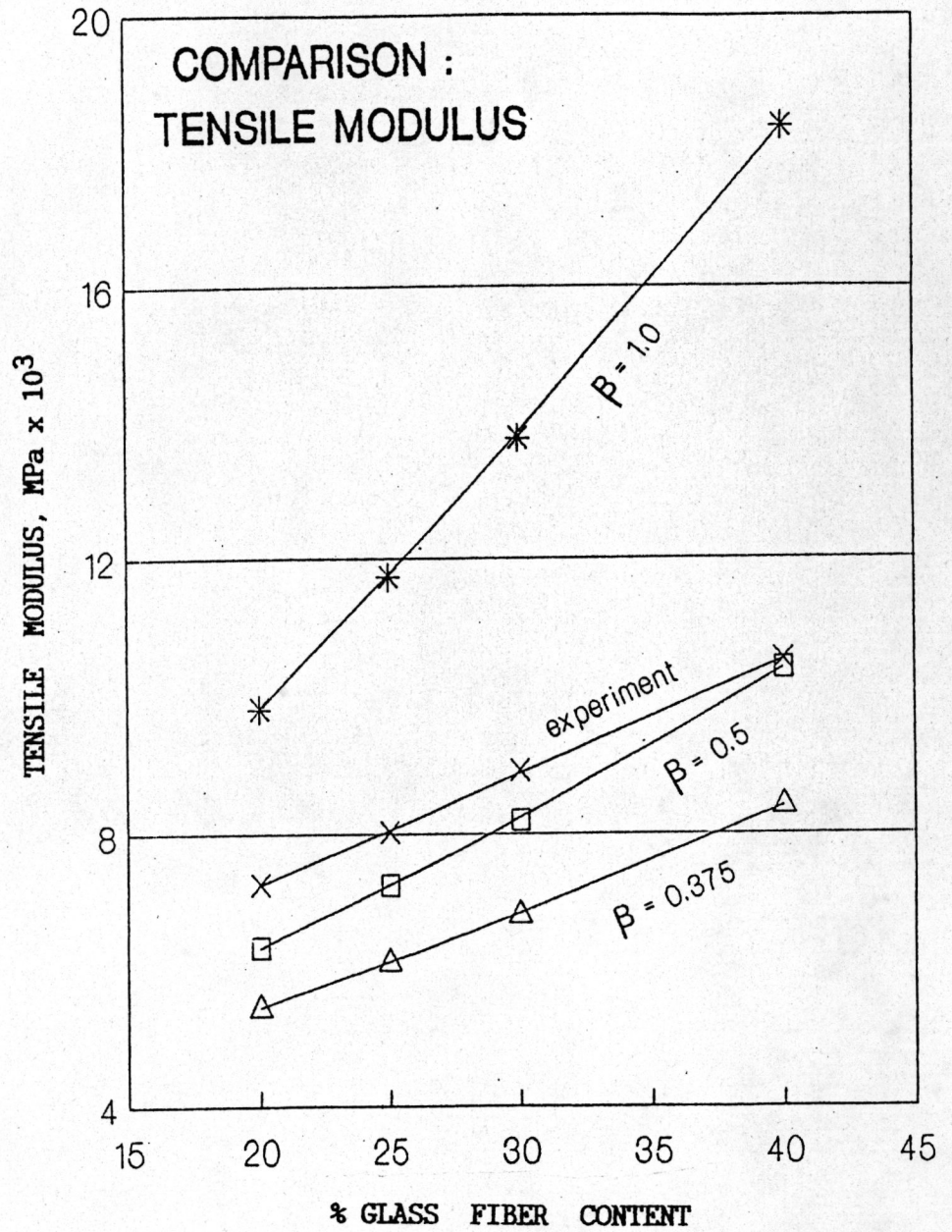


Figure 3.19 Comparison of tensile modulus between the calculated and the experimental results.

Table 3.3 Effect of the CaCO₃ and the glass fiber reinforcement on the mechanical properties of polyester SMC from the experimental results

Mechanical properties	% Glass fiber content (by weight, inclusive of 0 to 80% CaCO ₃ filler)			
	20%	25%	30%	40%
Tensile strength, MPa	63-82	83-107	97-137	134-182
Tensile modulus, MPa	7245-12185	8910-13380	9815-14295	10525-15300
Flexural strength, MPa	130-168	160-210	185-260	240-310
Flexural modulus, MPa	7270-11730	8490-13340	9765-14400	11584-17080
Impact strength, J/m	250-335	304-418	364-501	477-655

As regards the resin-to-glass ratio, the glass fiber is much stronger than the resin, so logically, the more proportion of glass fiber in composite, the greater the strength and modulus. There are practical limits to the amount of glass fiber 25-40% which can be used generate maximum strength with chopped strand mat in a hand-lay up process (22). However, in SMC process, the glass fiber may be used up to about 40-50 %, but it depends on the SMC compounding. In general, any lower resin content would not wet out the glass surface, and the higher resin content would merely represent excess resin and further loss of the mechanical properties.

3.3.2 Factors Influence Mechanical Properties of SMC : Micromechanics

3.3.2.1 Effect of Glass Fiber Reinforcement

Orientation of fibers with respect to the loading axis is an important parameter. The orientation directly affects the distribution of load between the fibers and the resin matrix. The contribution of the fibers to the composite properties is maximum only when they are parallel to the loading direction. The strength and modulus of composites will be reduced when the fibers are not parallel to the loading direction. In the experimental result for SMC, all the fibers were aligned randomly, the loads in some of the plies may not be in the fiber direction.

The stress-strain curves for general hypothetical composite materials with ductile and brittle fibers and a ductile matrix are shown in Figure 3.20 (21). The experimental results show in Figure 3.21, agree very well with that of the hypothetical composite. It is generally observed that the stress-strain curves of the composites fall between those of the fiber and matrix area.

For the effect of glass fibers on the strength of SMC, there are two possible causes for this variation: (i) it can occur as a result of variations in the fiber length with diameter resulting from the manufacturing process; and (ii) it can occur as a result of handling facility of fibers and from their surface treatment because of differences in the nature and intensity of chemical reaction at the coating-fiber interface. The chemicals used to treat the surface of glass fibers, greatly influence the curing behavior of polyester resin and consequently the mechanical and physical properties of fabricated products. By the characterization of the interface between E-glass fiber and unsaturated polyester resin matrix with the Fourier transform infrared (FTIR) spectroscopy, the silane coupling agents participate in the curing reaction of polyester resin, namely at the surface of the resin matrix, forming an interface, and that untreated E-glass inhibits the polymerization of unsaturated polyester resin (23). Between glass fiber and matrix of polyester resin, there is an interfacial bond of the glass fiber to resin

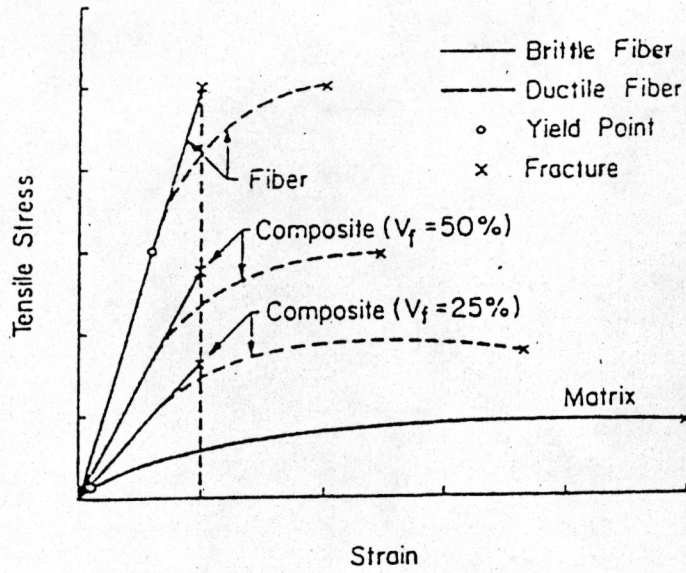


Figure 3.20 Stress-strain curves for hypothetical composite materials with ductile and brittle fibers and typical ductile matrix

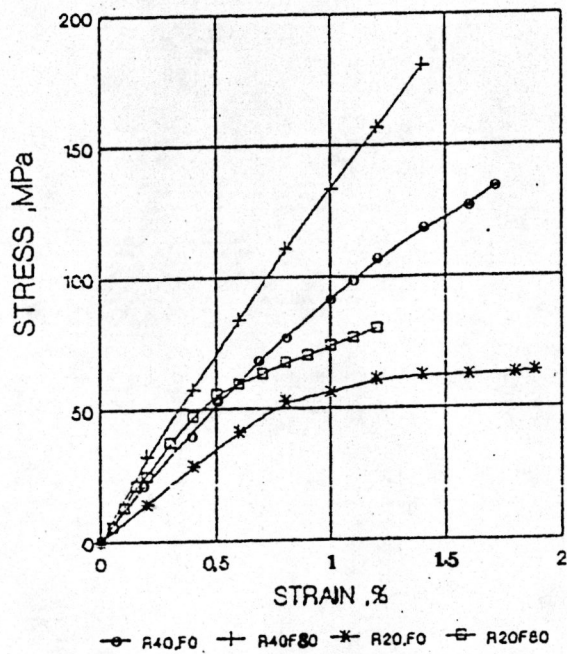


Figure 3.21 Stress-strain curves of the SMC under the effects of glass fiber reinforcement and CaCO_3 filler (R : glass fiber and F : CaCO_3)

described previously in the chemistry of silanecoupling agent in the section of INTRODUCTION. The scanning electron micrograph with represents the cross-sectional surface morphology of the sample (coded as R20,F0) of the binary resin-glass fiber system (no effect of CaCO_3 in the system) was shown in Figure 3.22. The picture shows the homogeneous compatibility between the surface of glass fiber and resin.

The interfacial bond between the matrix and the fibers is an important factor influencing the mechanical properties and performance of SMC products. The interface is responsible for transmitting the load from the resin to the fibers, which contributes to the greater strength of SMC. Thus the SMC strength is affected by the interfacial conditions. The mechanism of load transfer through the interface becomes more important to understand the mechanical failure of the SMC. The interfacial condition controls the mode of propagation of microcracks at the fiber ends (24). When a strong bond exists between the fibers and the matrix resin, the cracks do not propagate along the length of the fibers. Thus the fiber reinforcement remains effective even after the fiber breaks at several points along its length. Such a situation is well explained by the model of microcracking in Figure 3.23. A strong bond is also essential, the effect to such an environmental performance becomes severe if the adhesion is inadequate especially when the SMC is under load and utilized as structural SMC application(25).

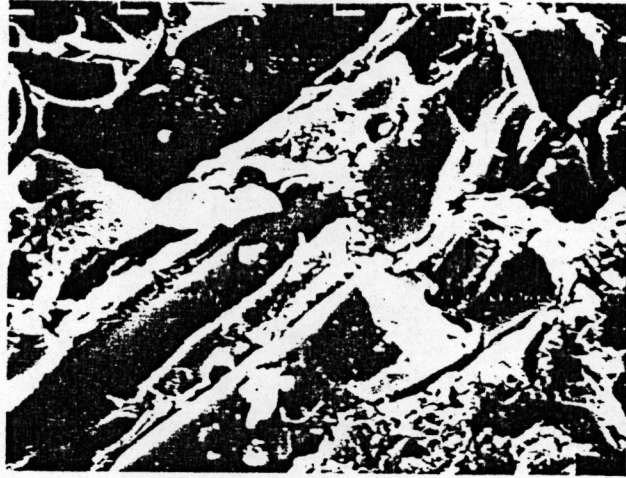


Figure 3.22 Electron micrograph of the cross-sectional surface morphology of the sample (R20,F0) of resin-glass fiber system.

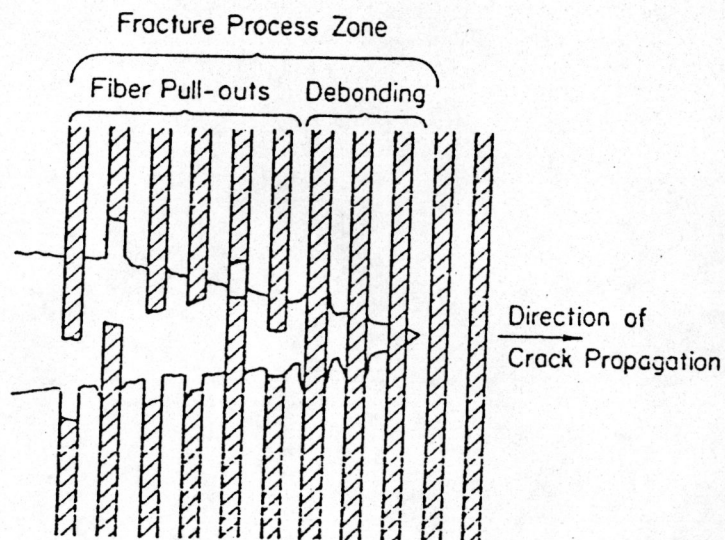


Figure 3.23 Model of microcrack tip in the fiber composites.

Since the load is not directly applied to the fibers, but to the matrix resin which is transferred to the fibers through the small fiber. The stress on a continuous fiber can be assumed constant over its entire length (21). An important consideration in the behavior of chopped fiber, especially to SMC is that the fiber ends cause stress concentrations.

This is particularly important in the case of the failure of SMC with brittle matrices. As a result of the stress concentrations, the fiber ends get separated from the matrix at a very small load, thus producing a microcrack in the matrix. However, noted that the first microcrack at the fiber end may be resulted in several alternate effects, such as the shear stress, the impact stress or the environment attack (26). When this happens, the interface may separate the fiber from the matrix by propagating the crack along the length of the fiber, and then the fiber becomes totally ineffective and the composite is acting as if it were a bundle of fibers. For this case, the strength of the composite is not enhanced by the presence of the matrix resin. Alternatively, the crack may propagate out in a direction normal to the fibers across the other fibers, as a result of the local stress concentrations, leading to immediate composite fracture (27). If both of these crack-propagation effects are suppressed, an increased load results in further separation of fiber ends from the matrix, such as an example of fracture cracking which is illustrated in Figure 3.24.



(a)



(b)



(c)

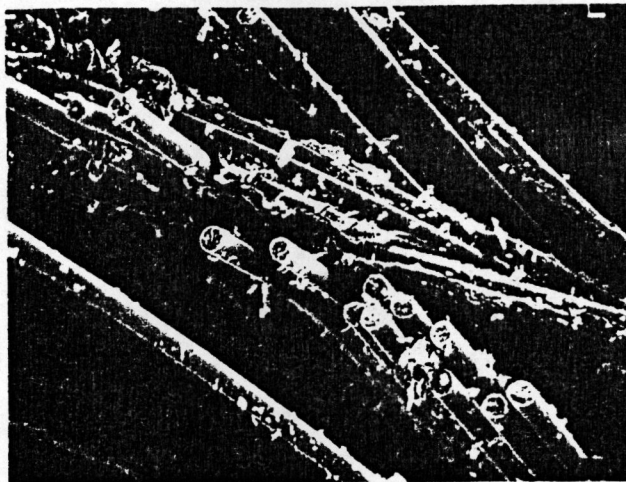
Figure 3.24 Electron micrographs (35x) show the continuous fracture during deformation from flexural test:
(a) at initial cracking state
(b) at in the later state and
(c) at ultimate fracture cracking state.

Furthermore, the electron micrograph of the SMC sample (R20, FO) in Figure 3.25 which was subjected to the tensile load, shows the fracture surface of fiber separated from the matrix resin; in (a) random direction of fibers is pulled out (350 x) and (b) 1500 times amgnification of the same sample.

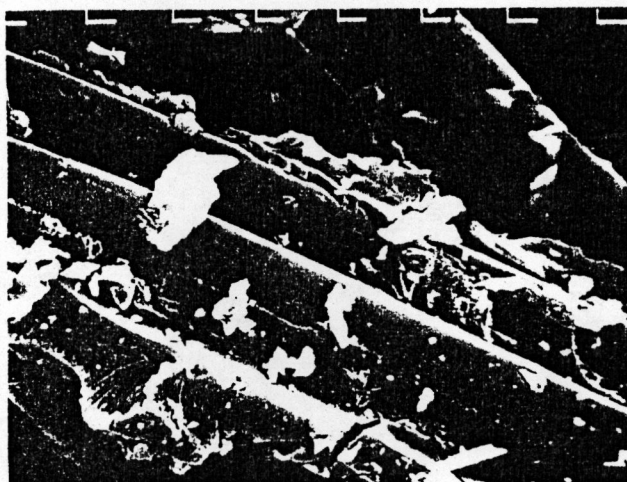
3.3.2.2 Effect of CaCO_3 Filler

According to the experimental results, CaCO_3 as the filler can produce specific improvements in certain mechanical properties, i.e. both an increase in tensile strength and in flexural modulus. The use of CaCO_3 results in product properties with higher stiffness and dimensional stability at shorter cycle times. However, the high stiffness is not obtained at the high degree of CaCO_3 filler when it is compared with that of the glass fiber reinforcement.

From the experiment, the use of surface-treated CaCO_3 results in better mechanical properties, in particular, improves flexural modulus, however it does not affect so much in strength. In contrast to the percentage of elongation, shrinkage and stress cracking are reduced by the CaCO_3 content. It can decrease the crack tendency in the SMC products and improves impact resistance and surface quality.



(a)



(b)

Figure 3.25 Electron micrograph of SMC (R 20, F-0) failed under tensile load, shows the fracture surface of fiber separated from the matrix resin:

- (a) random direction of fiber pullout (350x) and
- (b) a close-up electron micrograph (1500x) at the separation of surface cracking.

As a result of a good dispersion, the particular treated CaCO_3 also influences the mechanical properties. The homogeneous dispersion of the treated CaCO_3 with the resin can be visualized by scanning electron micrograph as shown in Figures 3.26 -3.29. Figure 3.26 illustrates the single phase of resin matrix without CaCO_3 . In these figures, the treated CaCO_3 as a particulate phase can be found uniformly in the matrix phase even if they were pulled out under tensile loads. The function of the treated filler in this system, may act mainly through the volume that it takes up. In the presence of the treated CaCO_3 , the resin-matrix segments are attached to the CaCO_3 surface by secondary or primary valence bonds (28) in turn cause a certain immobilization of adjacent segments and a possible orientation of the resin matrix. The reason for this immobilization lies in the high degree of dimensional stability of the treated CaCO_3 particles.

A homogeneous distribution of treated CaCO_3 in the matrix phase is basically important in SMC compound. The free surface energy and the polarity of the bond between CaCO_3 and matrix are also important factors in this regard. Noted that the surface of CaCO_3 was treated with 1% of stearic acid, it should be considered that a lipophilic character can be imparted to each other. This interaction may occur between the surfaces of CaCO_3 filler and the polyester resin which is connected through a structural long chain of stearic acid; R or $\text{CH}_3-(\text{CH}_2)_{16}$ by the physical bonding in

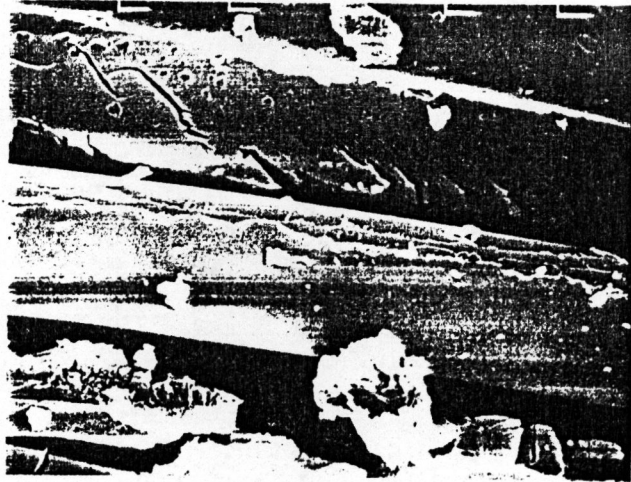


Figure 3.26 Electron micrograph (at 2000 x) of the cross-sectional area from the fracture surface of tensile loading, of SMC sample, 20% glass fiber and without CaCO_3 (R20,FO).

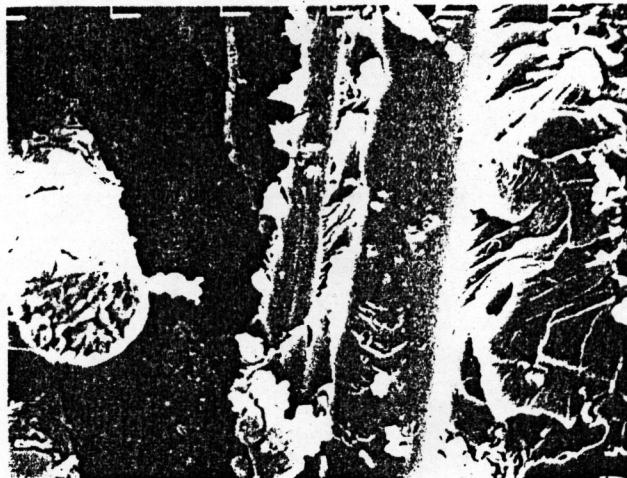


Figure 3.27 Electron micrograph (at 2000 x) of the cross-sectional area from the fracture surface of tensile loading, of SMC sample, 20% glass fiber and 20% CaCO_3 (R20,F20).



Figure 3.28 Electron micrograph (at 2000 x) of the cross-sectional area from the fracture surface of tensile loading, of SMC sample, 20% glass fiber and 40% CaCO_3 (R20,F40).

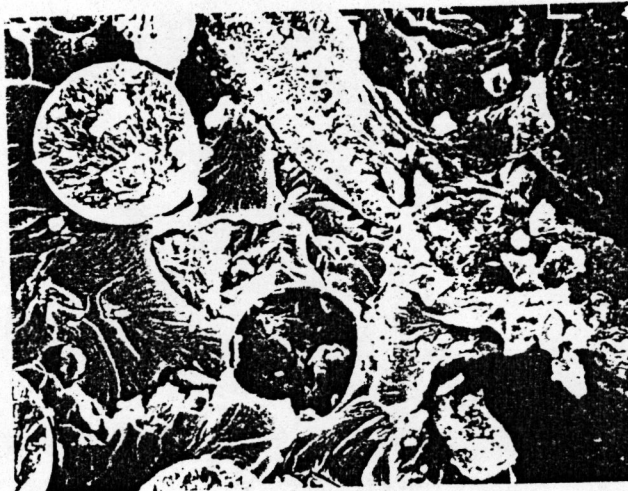


Figure 3.29 Electron micrograph (at 2000 x) of the cross-sectional area from the fracture surface of tensile loading of SMC sample, 20% glass fiber and 80% CaCO_3 (R20,F80).

the intermolecular chain of cured SMC. Accordingly, the previously proposed mechanisms can explain the effects of CaCO_3 filler on mechanical properties, in that it provides high strength and modulus as well as improved performance during processing of the SMC.