

## CHAPTER IV

### RESULTS AND DISCUSSIONS

#### 4.1 Effect of the Catalysts on Hardening Characteristics of the Resin

To measure hardening characteristics of the resin containing different types and various concentrations of catalysts, one can use the ASTM D2471-71 (18) and JIS K 6901 (19) test methods. The former is for the determination of gel time and the peak of exothermic temperature of reacting thermosetting resin, while the latter is for those of liquid unsaturated polyester resins. These test methods cover the determination of the time starting from mixing the reactants including the catalysts to start the reaction at 150°C, to the time when solidification commences or the resin mix is completely cured. The above mentioned ASTM test method also provides a means for measuring the maximum temperature reached by a reacting thermosetting plastic composition; as well as for the time from an initial reaction to the time when the peak of an exothermic temperature was reached by measuring the relationship between time and exothermic heat of the curing reaction in a form of a rapid increase in temperature when the resin

was completely cured. It is clear by inspection of the curve that these regions are well defined. The division of the regions is useful for characterizing the thermal response of a curing process.

Regarding the type and concentration of the catalysts used for curing the polyester resin, hardening characteristics of the resin at 150°C, influenced by the catalysts : the TBPB, DTBC, BPO, and the mixture of TBPB and PBQ are presented in Figures 4.1-4.4, respectively.

The TBPB catalyst has a half-life temperature, i.e., the temperature at which the peroxide is 50% decomposed in 10 hours at 104°C; while those of the DTBC and the BPO are at 93 and 73°C, respectively. In principle, the peroxide half-lives usually are determined in solvent and the half-life temperature data are useful for comparing the activity of one peroxide against another and therefore it is often used as a basis for initial catalyst screening. For example, a "hot" catalyst with a lower half-life temperature will give a shorter curing time in the SMC process at elevated molding temperatures than a catalyst with a higher half-life temperature (1). The PBQ inhibitor added into unsaturated systems for the prevention of a measurable amount of polymer formation is widely practiced. However, in unsaturated polyester resins, they function other than to prolong storage life and to prevent undesirable changes in the gel time on long term storage.

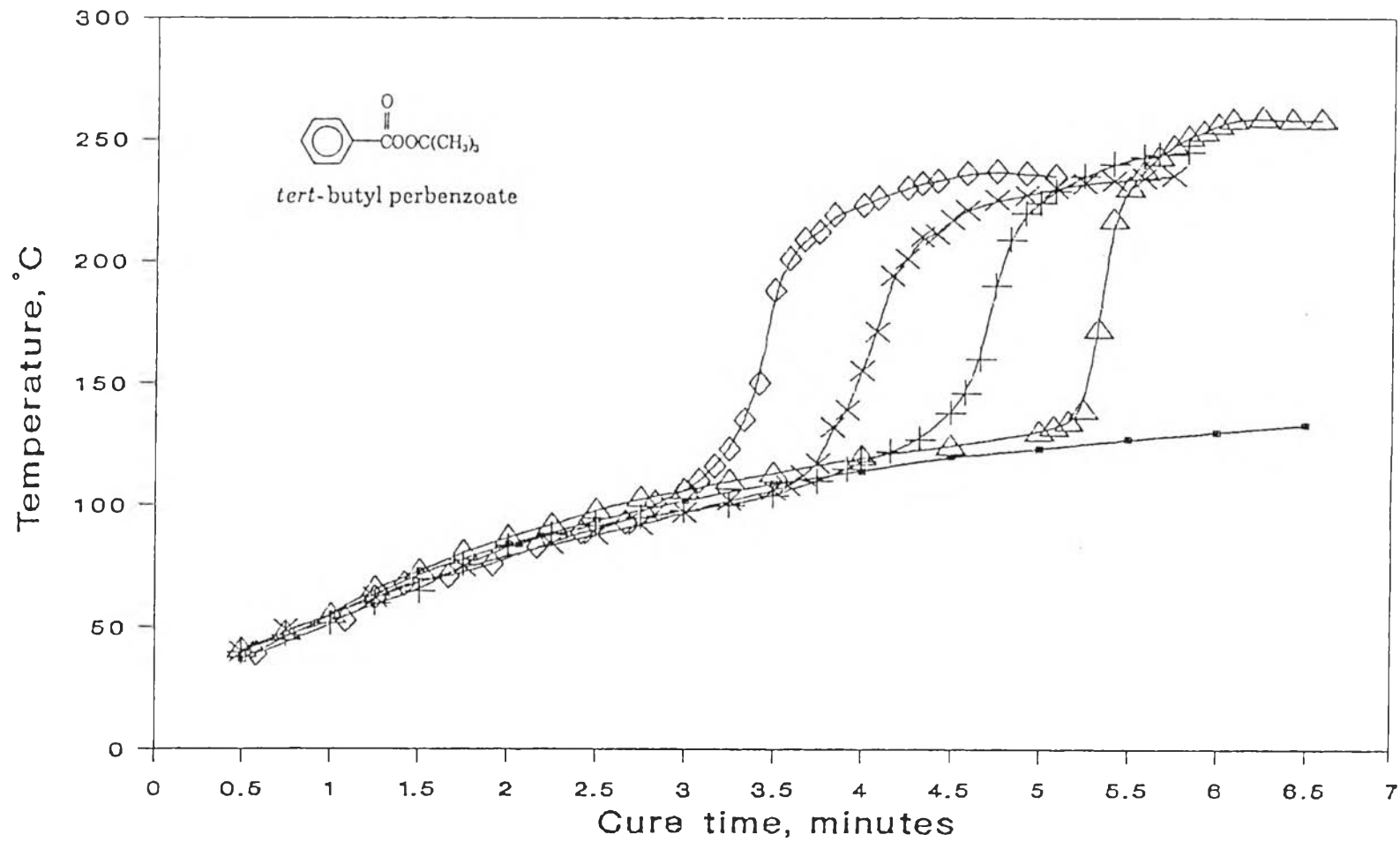


Figure 4.1 Concentration effect of TBPB on hardening time of the resin. ( —■— Resin, —+— 1 phr, —\*— 2 phr, —◇— 3 phr, —△— 2 phr added PBQ 0.05 phr.)

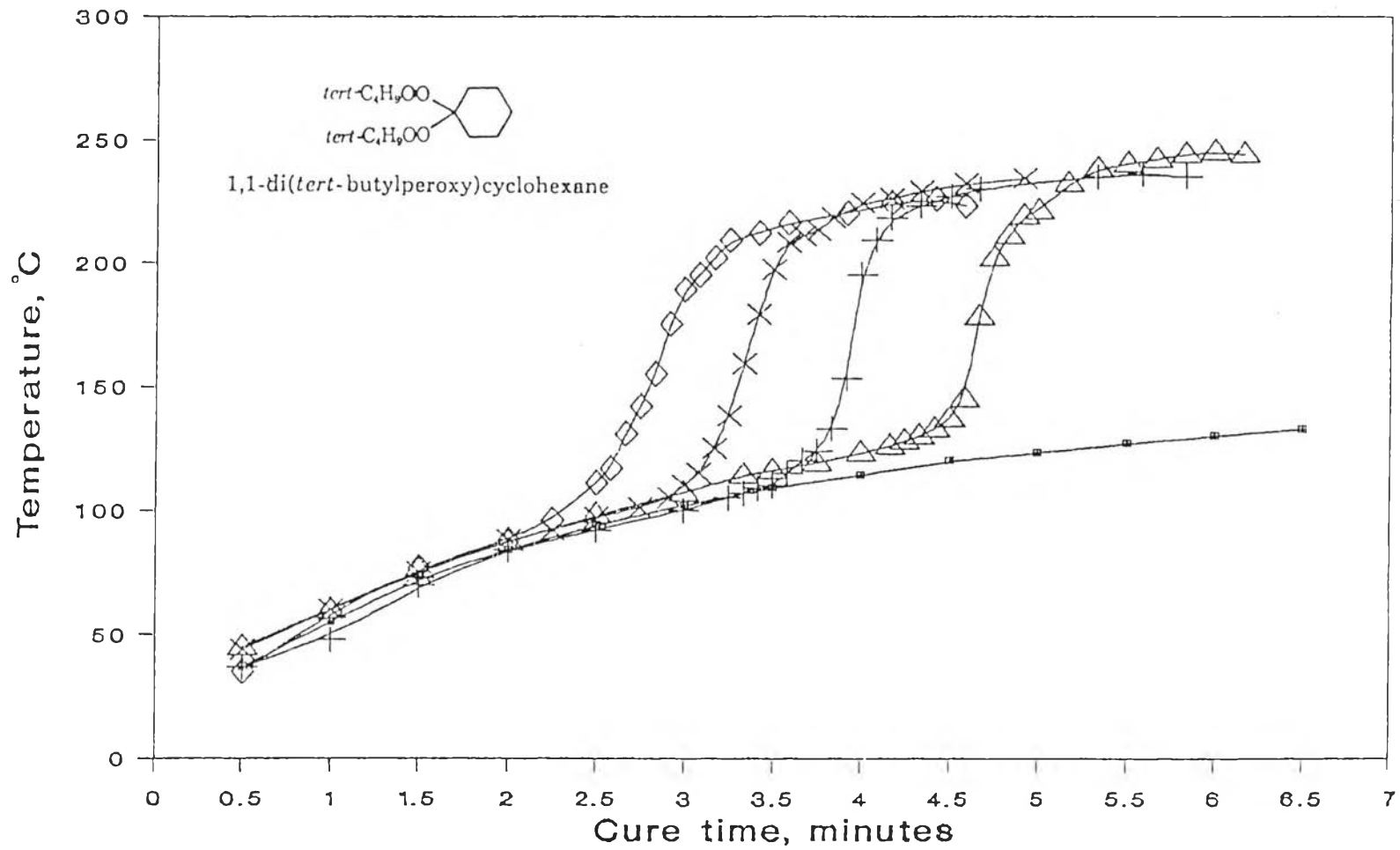


Figure 4.2 Concentration effect of DTBC on hardening time of the resin. ( —■— Resin, —+— 1 phr, —×— 2 phr, —◇— 3 phr, —△— 2 phr added PBQ 0.025 phr.)

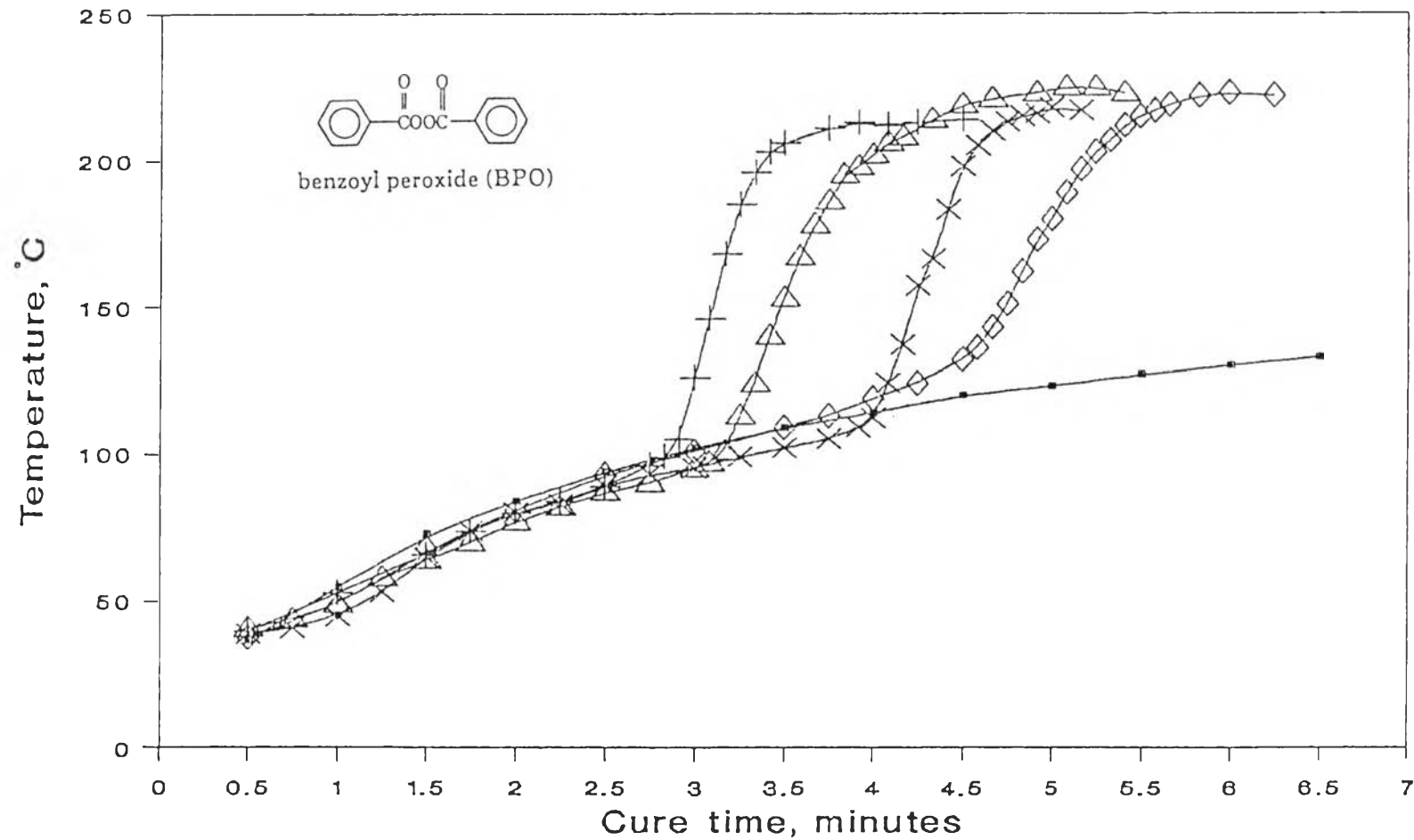


Figure 4.3 Concentration effect of BPO on hardening time of the resin. ( —■— Resin, —◇— 0.05 phr, —×— 0.5 phr, —△— 1 phr, —+— 2 phr.)

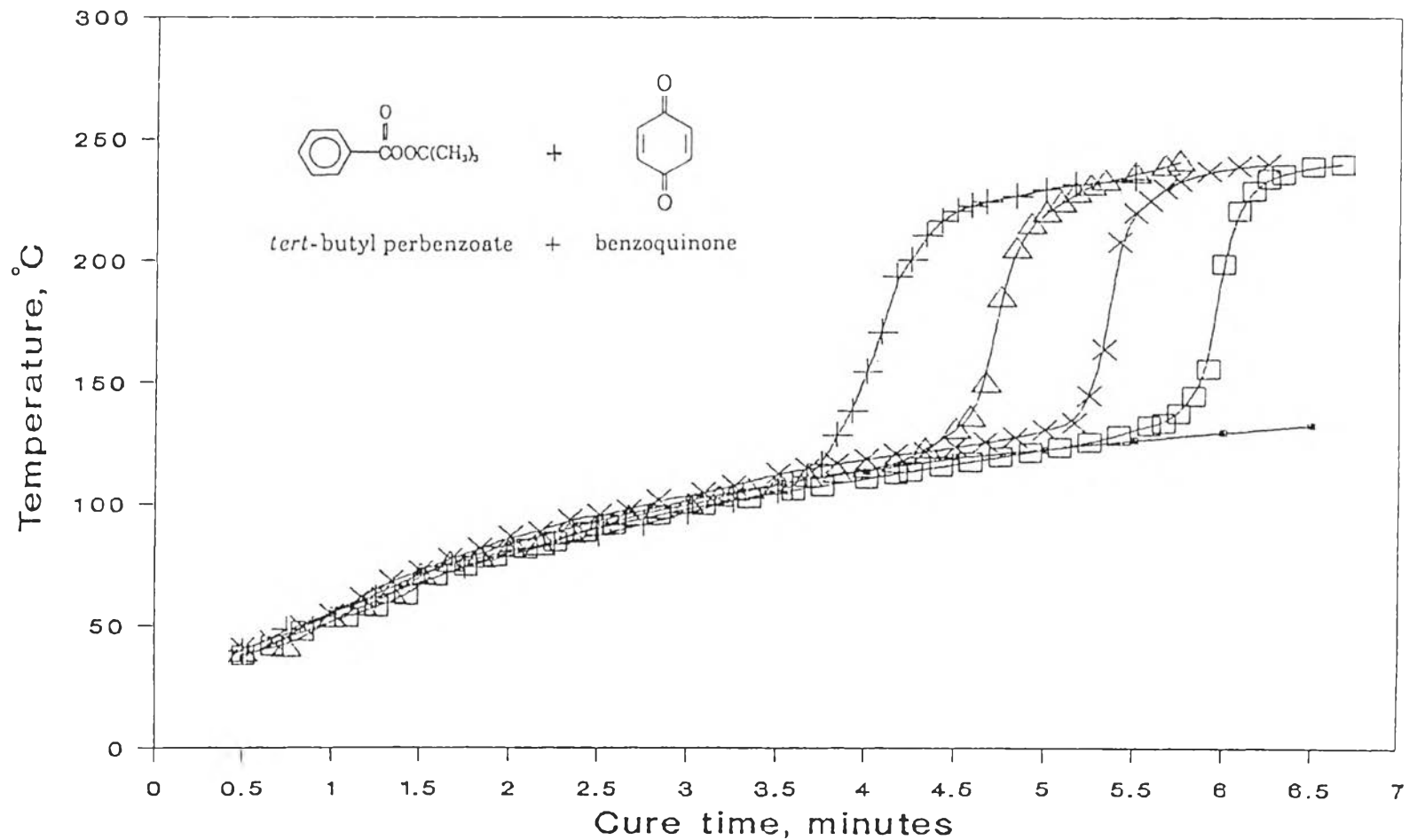


Figure 4.4 Combined effect of the added PBQ influencing TBPB on hardening time of the resin. ( — Resin, —+— TBPB 2 phr; —△— added PBQ 0.025 phr, —×— added PBQ 0.050 phr, —□— added PBQ 0.075 phr.)

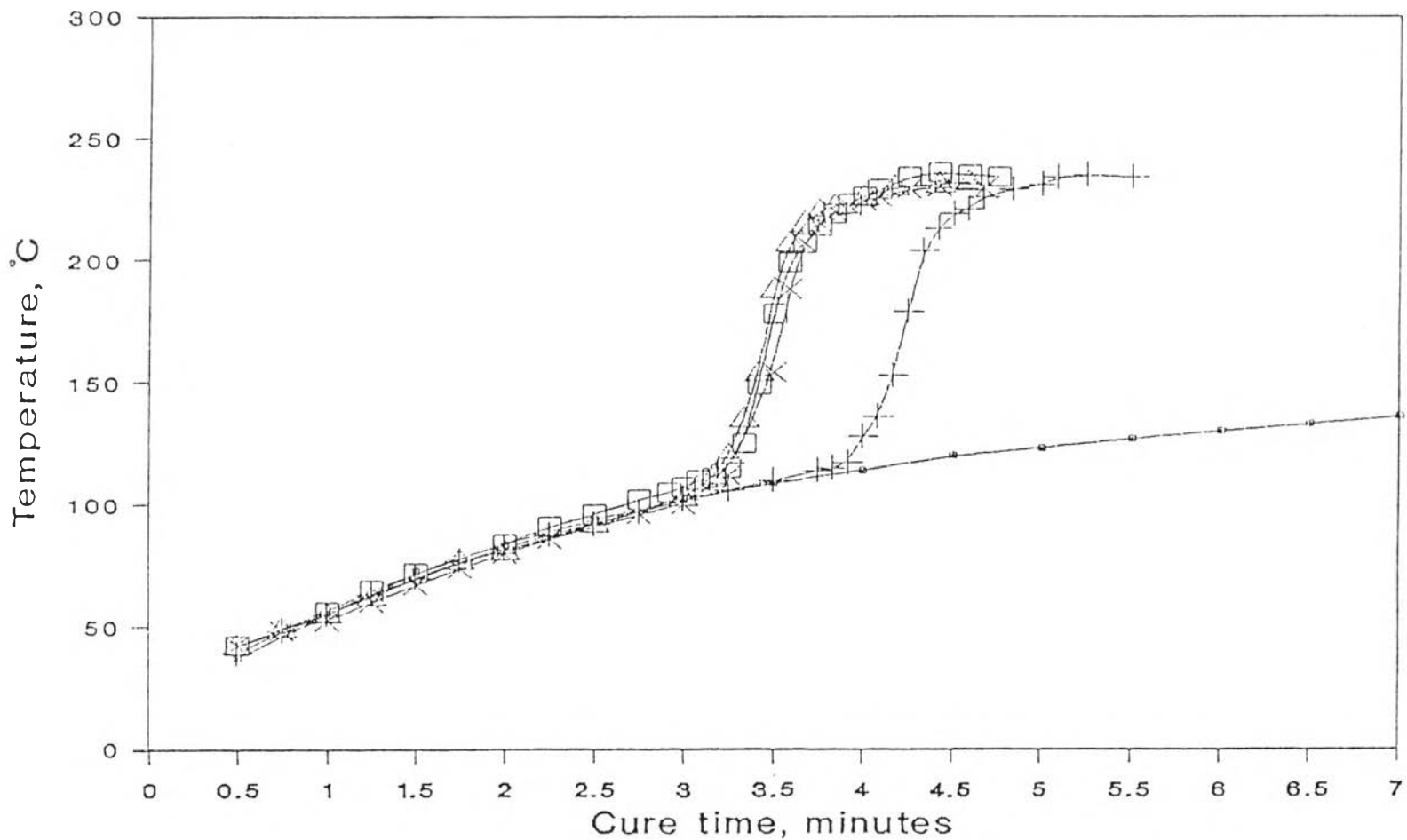
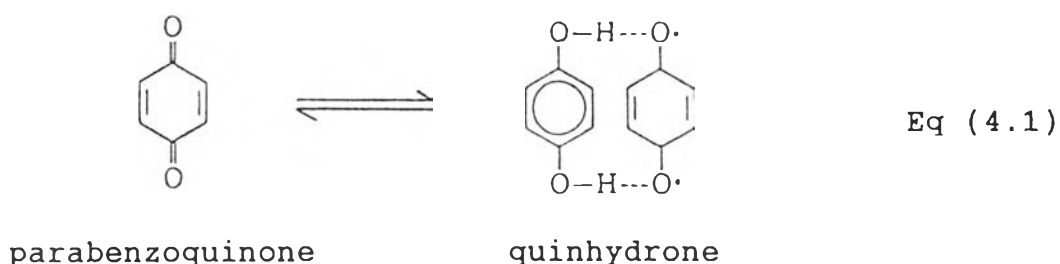


Figure 4.5 Dual catalytic effect of the dual catalysts of TBPB and DTBC on hardening time of the resin. ( —•— Resin, —+— 0.5 phr : 0.5 phr, —△— 1.5 phr : 1.5 phr, —□— 1.0 phr : 1.0 phr, —×— 0.5 phr : 0.5 phr.)

From the results in Figures 4.1-4.3, we could conclude that the hardening time of the resin depended greatly on the type and quantity of the catalysts. As predicted, the hardening times were found to be shorter for the catalyst with a lower half-life temperature. On considering the effect of equal quantity of each catalyst on curing time, the BPO catalyst gave the shorter curing time than those of the DTBC and TBPB, respectively.

When 2 phr of the TBPB was incorporated the unsaturated polyester resin, an addition of the PBQ inhibitor adversely affected the curing time of the resin. The PBQ inhibitor which had been reported as giving good room temperature pot lives, was then included in the list of screening consideration. A formulation containing parabenzquinone (PBQ) was also included since it was commonly added to the catalyst package to extend the shelf life of the compound. Results are shown in Figure 4.4. As expected, the PBQ catalyst retarded the curing mechanism from which a longer curing time is needed. The mechanistic schemes for the inhibitory action of parabenzquinones have been elucidated as follows (11):





The quinhydrones act as free-radical scavengers or stabilizers with chain carrying free radicals to form inert products in one of termination steps.

To reduce the curing time over what can be obtained with a singly heat-activated catalyst, dual catalyst systems are often employed. One of the more common SMC catalyst combinations today is t-butyl peroctoate (TBPO) used in conjunction with t-butyl perbenzoate (TBPB). Various combinations of these two catalysts were investigated. The dual catalyst system was indeed found to be faster than the TBPB alone (1).

In case of the dual catalyst between TBPB and DTBC shown in Figure 4.5, the difference of hardening time of the resin could be summarized as follows:

1. When enough quantities of both catalysts were mixed, a reduced curing time of the resin could be observed. In this particular case, the ratio of both catalysts at 1:1 was considered the best choice as it gave a shorter curing time.

2. The effect of the DTBC catalyst on curing time of the resin was greater than that of the TBPB catalyst.

Table 4.1 shows the hardening time of the respective catalysts obtained by the intersection between the slop and the shoulder of the curve. Increasing the quantities of the catalyst, hardening time was gradually shortened as illustrated in Figure 4.6. But in case of adding the PBQ inhibitor, increasing the quantities of the PBQ, the hardening time was gradually extended as shown in Figure 4.7.

From the result in Table 4.1, the structural differences of the peroxide catalysts that affect the nonpromoted activity of peroxides are related to three factors: the relative stability of the radicals formed, i.e., the more stable the radical that is formed, the less stable the peroxide; the steric factors, i.e., highly strained peroxides are less stable since decomposition relieves the steric strain; and the electronic effects where, e.g., electron-donating functions generally destabilize and electron-withdrawing functions stabilize peroxides (8).

The TBPB catalyst is a type of peroxyester and its 10-h half-life temperature (determined in 0.2 M benzene) is 104°C. This peroxide cleaves at the oxygen-oxygen bond to supposedly generate acyloxy and alkoxy radicals:

Table 4.1

Effect of the type and concentration of the catalysts  
on the hardening time of the catalyst.

Concentration of the Catalyst (phr)				Hardening Time (minutes)
TBPB	DTBC	BPO	PBQ	
1	—	—	—	4.37
2	—	—	—	3.43
3	—	—	—	3.25
—	1	—	—	3.44
—	2	—	—	3.07
—	3	—	—	2.41
—	—	0.05	—	4.20
—	—	0.5	—	3.59
—	—	1.0	—	3.09
—	—	2.0	—	2.52
2	—	0.05	—	3.36
0.5	0.5	—	—	4.04
0.5	1.5	—	—	3.20
1.0	1.0	—	—	3.14
1.5	0.5	—	—	3.16
2	—	—	0.025	4.36
2	—	—	0.050	5.15
2	—	—	0.075	5.51
—	2	—	0.025	4.34

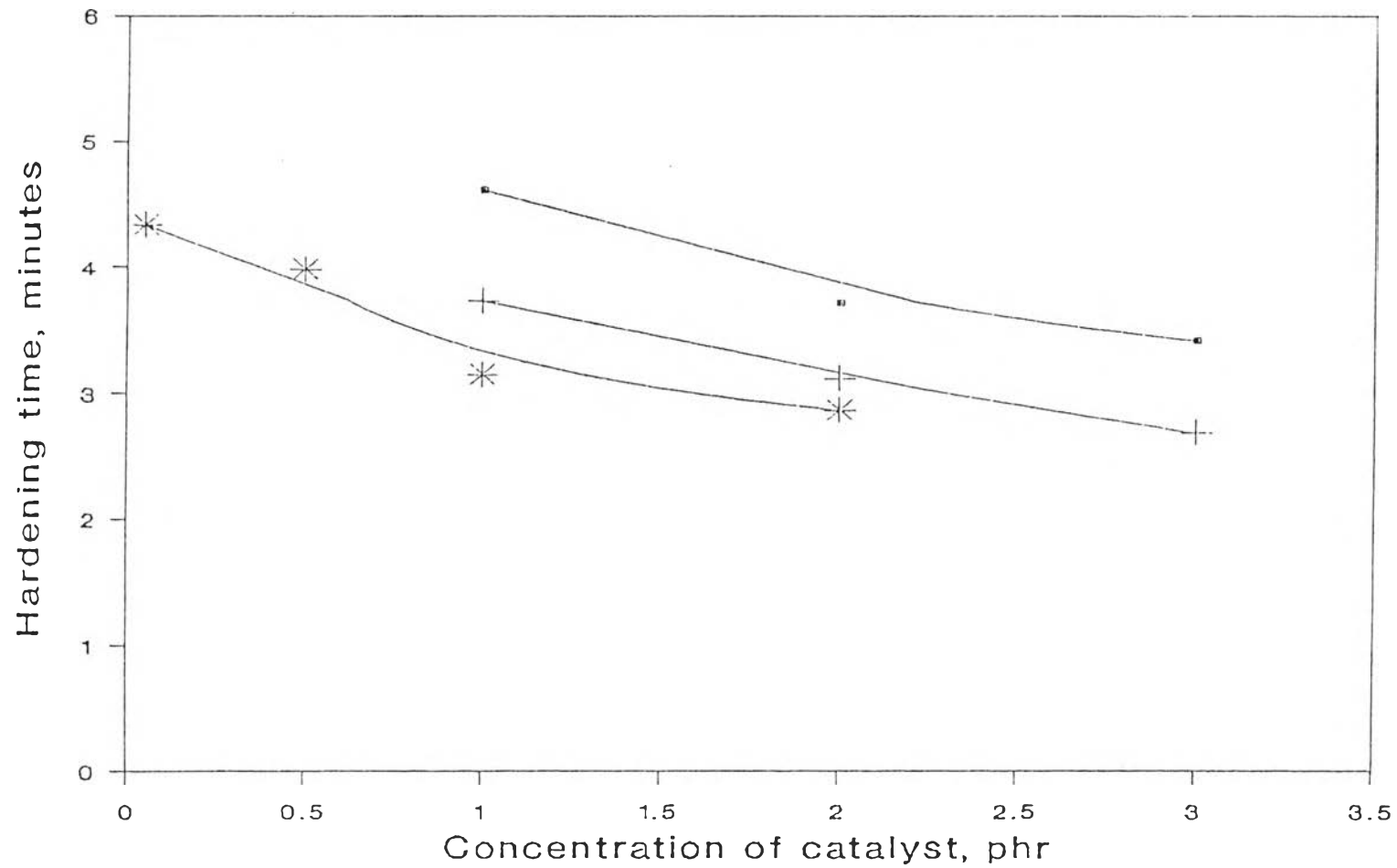


Figure 4.6 Effect of different catalysts on hardening time of the resin. ( —●— TBPB, —+— DTBC, —\*— BPO.)

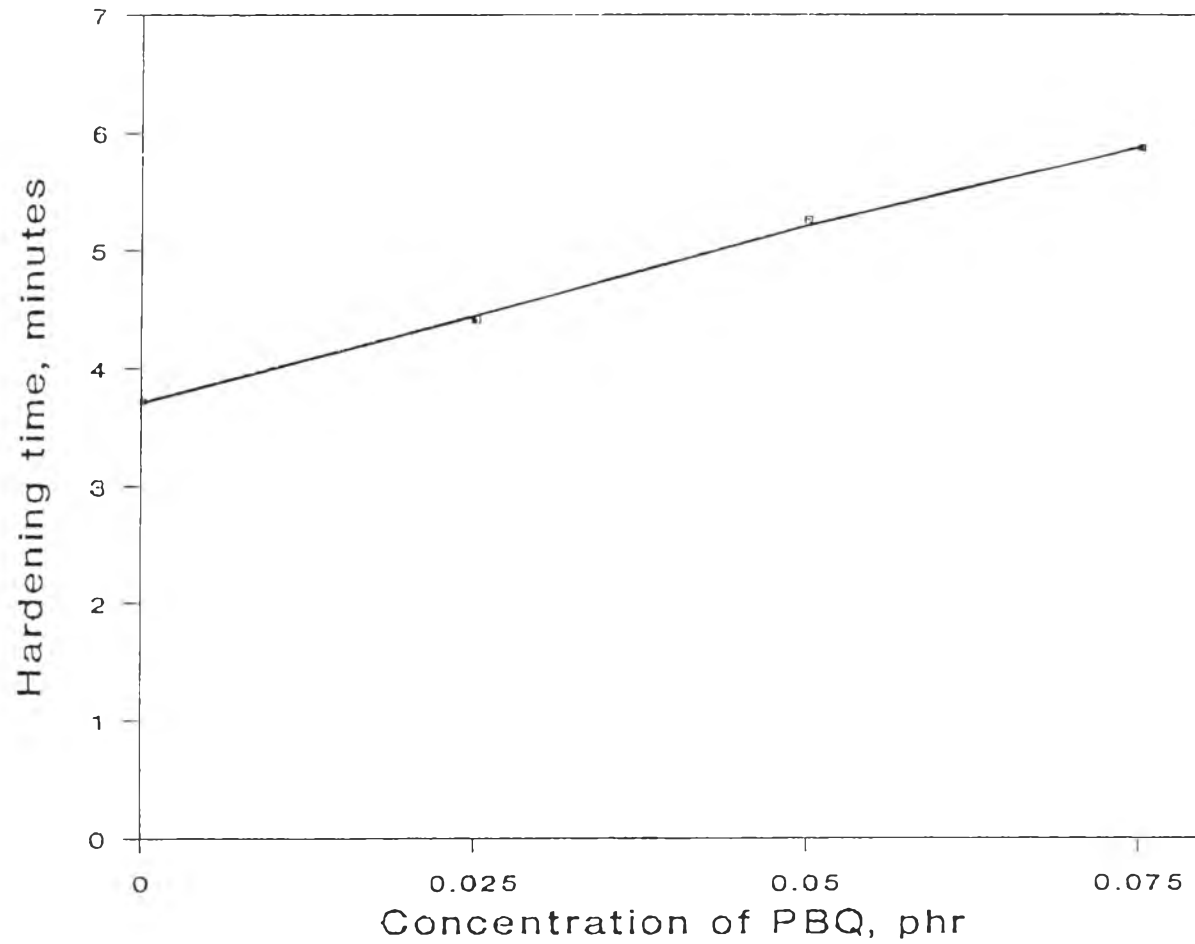
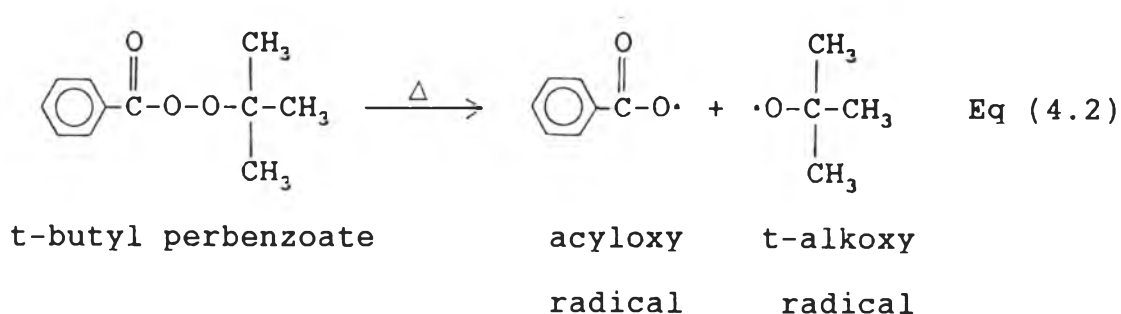
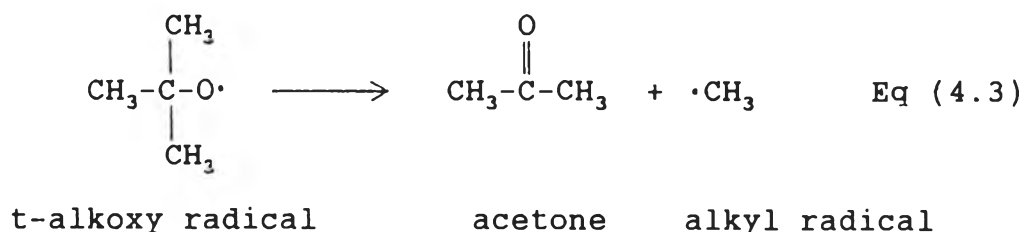


Figure 4.7 Effect of the parabenzoquinone inhibitor (PBQ) added in the 2 phr TBPB catalyst containing resin on hardening time of the resin.

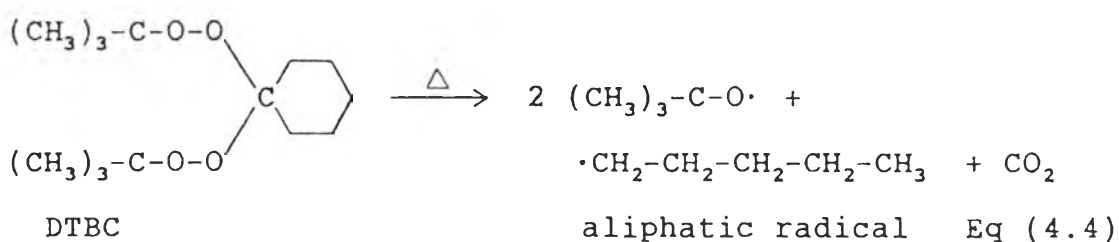


The acyloxy radical can decarboxylate as noted above. Only tertiary alkyl peroxyesters are available commercially and, consequently, only tertiary alkoxy radicals are generated. Alkoxy radicals can undergo a beta-scission reaction:

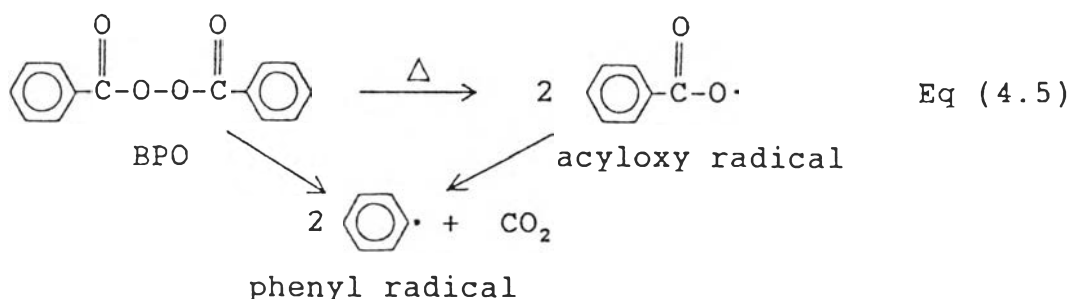


One of the  $-\text{CH}_3$  groups splits off to form a ketone and a new alkyl radical. The group that splits off is the one that forms the most stable radical. If the radical that splits off is more stable than the alkoxy radical, the beta-scission reaction will be fast and the predominant initiating species may be the alkyl radical rather than the alkoxy radical. The beta-scission reaction also is temperature-dependent, i.e., more scission occurs if the alkoxy radical is generated at high temperatures (8).

The DTBC catalyst is di-(tert-butylperoxy) ketal, and its 10-h half-life temperature (determined in 0.2 M benzene) is 93°C. This diperoxy compound decomposes thermally to produce three radicals, two of which can be a tertiary alkoxy radical.



The benzoyl peroxide catalyst is diacyl peroxide, and its 10-h half-life temperature (determined in 0.2 M benzene) is 73°C. Although this peroxide cleaves at the oxygen-oxygen bond, other bond cleavages (decarboxylations) can and do occur either simultaneously or sequentially to render an oxygen-oxygen bond breaking:



The rate of decarboxylation primarily depends upon temperature, pressure, and the stability of the acyloxy radical formed. The more stable the radical, the faster the decarboxylation and, with many diacyl peroxides, it

occurs simultaneously with an oxygen-oxygen bond breaking. (because of the high reactivity of the corresponding decarboxylated methyl and phenyl radicals). Diacyl peroxides that are derived from nonalpha-branched carboxylic acids may also form acyloxy radicals initially, but they decarboxylate extremely fast and evidence for their formation is not conclusive (8).

According to the above equations, the TBPB catalyst can produce one acyloxy and t-alkoxy radicals whereas the DTBC catalyst produces two t-alkoxy radicals and one aliphatic radical; the BPO catalyst only gives two acyloxy radicals. The number of the radicals produced is the main attribute to the different curing characteristics of the resin.

The relative stability of radicals which can be correlated with the t-alkyl radicals are more stable than secondary alkyl radicals and consequently the latter are more stable than primary alkyl radicals, and of course the hydroxyl radical is the most active. The methyl radical is more reactive than other primary alkyl radicals and is almost as reactive as alkoxy radicals. This is another important consideration in designing or choosing a peroxide initiator (8). Thus, the rate of dissociation of the BPO was reactive than those of the DTBC and TBPB, respectively.



## 4.2 Effect of the Catalysts on Curing Time Through the Curing Reaction of the Resin

The infrared spectroscopic technique was used as a tool to follow up changes before and after curing reactions of the resin in various forms and conditions by considering the strong band at  $1730\text{ cm}^{-1}$  corresponding to the carbonyl stretching. It was assumed that the bands at  $1730\text{ cm}^{-1}$  remain unchanged during cure because the carbonyl or ester groups in the polyester chain are virtually constant during polymerization. The medium absorption bands at  $1648\text{ cm}^{-1}$  and  $1634\text{ cm}^{-1}$  were assigned to the C=C stretching from the styrene and maleic anhydride, respectively. The bands at  $915\text{ cm}^{-1}$  are related to the -CH=CH- absorption due to the styrene. The bands at  $982/992\text{ cm}^{-1}$  correspond to the absorption of both styrene and polyester double bonds (4).

### 4.2.1 Evidence of the Curing Reaction in the Polyester Resin in the Presence of the Catalysts

Figures 4.8-4.10 show the comparative spectra of the unsaturated polyester resins, before and after curing reactions at  $150^{\circ}\text{C}$  for 2 minutes, in the presence of the 2 phr TBPB, 2 phr DTBC and 1 phr BPO catalysts, respectively. The major change in the spectra is the tremendous decrease in the absorption intensity for the  $1648\text{-}1634\text{ cm}^{-1}$ ,  $985\text{ cm}^{-1}$ , and  $915\text{ cm}^{-1}$  band, which is the

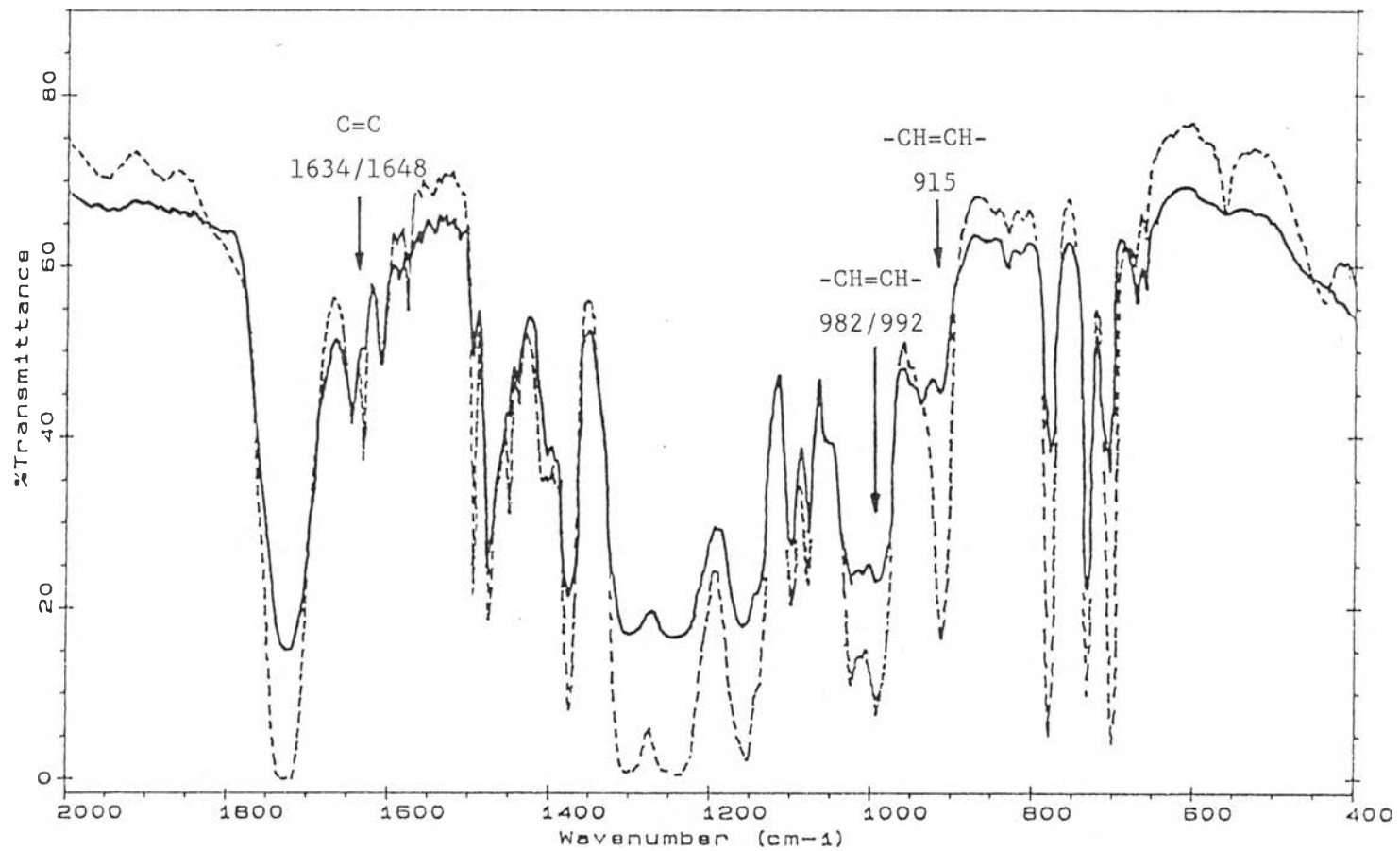


Figure 4.8 The infrared spectra of the polyester resins mixed with 2 phr of the TBPB catalyst before the curing reaction and after the curing reaction at 150°C for 2 minutes. (----- before curing, ——— after curing.)

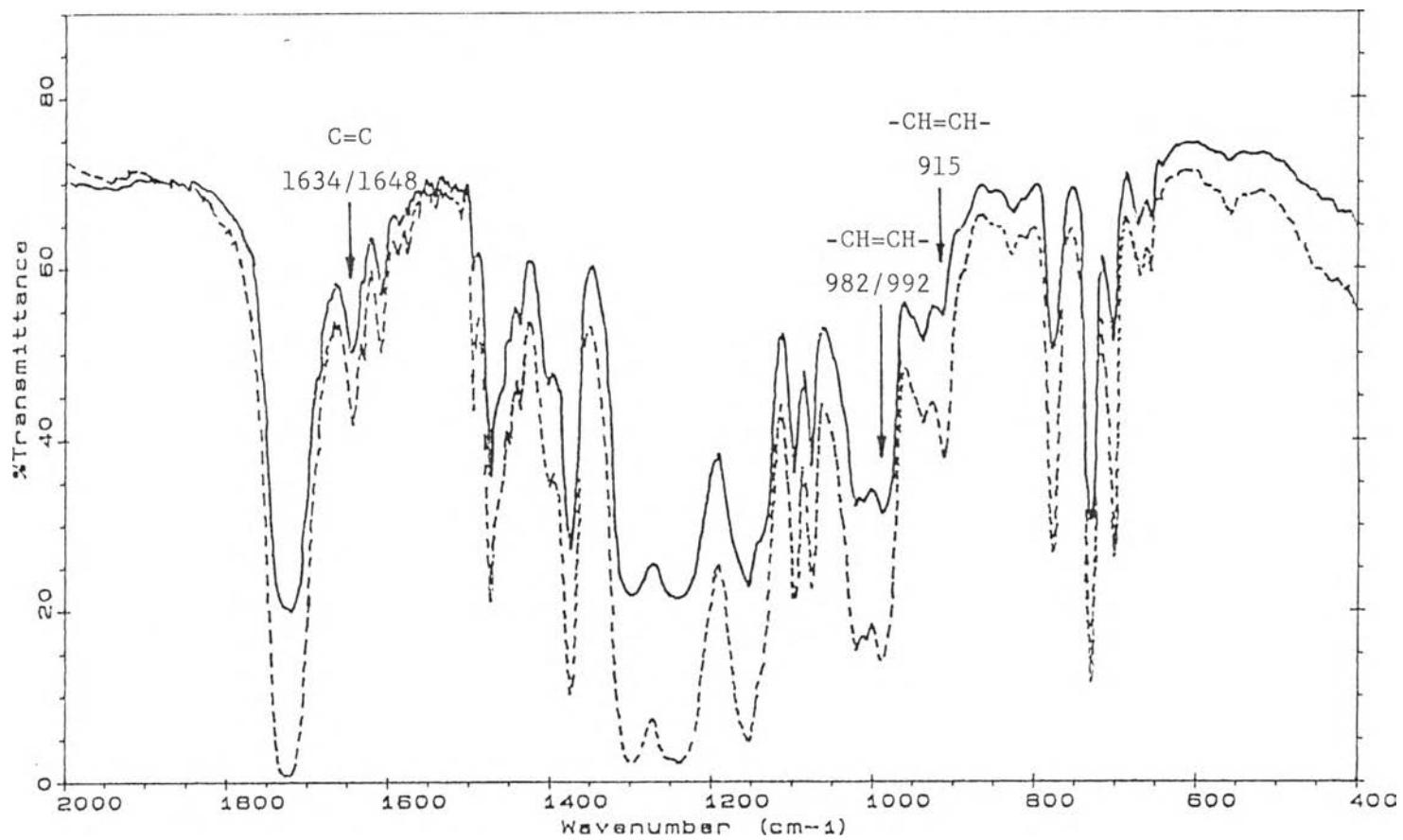


Figure 4.9 The infrared spectra of the polyester resins mixed with 2 phr of the DTBC catalyst before the curing reaction and after the curing reaction at 150°C for 2 minutes. (----- before curing, ——— after curing.)

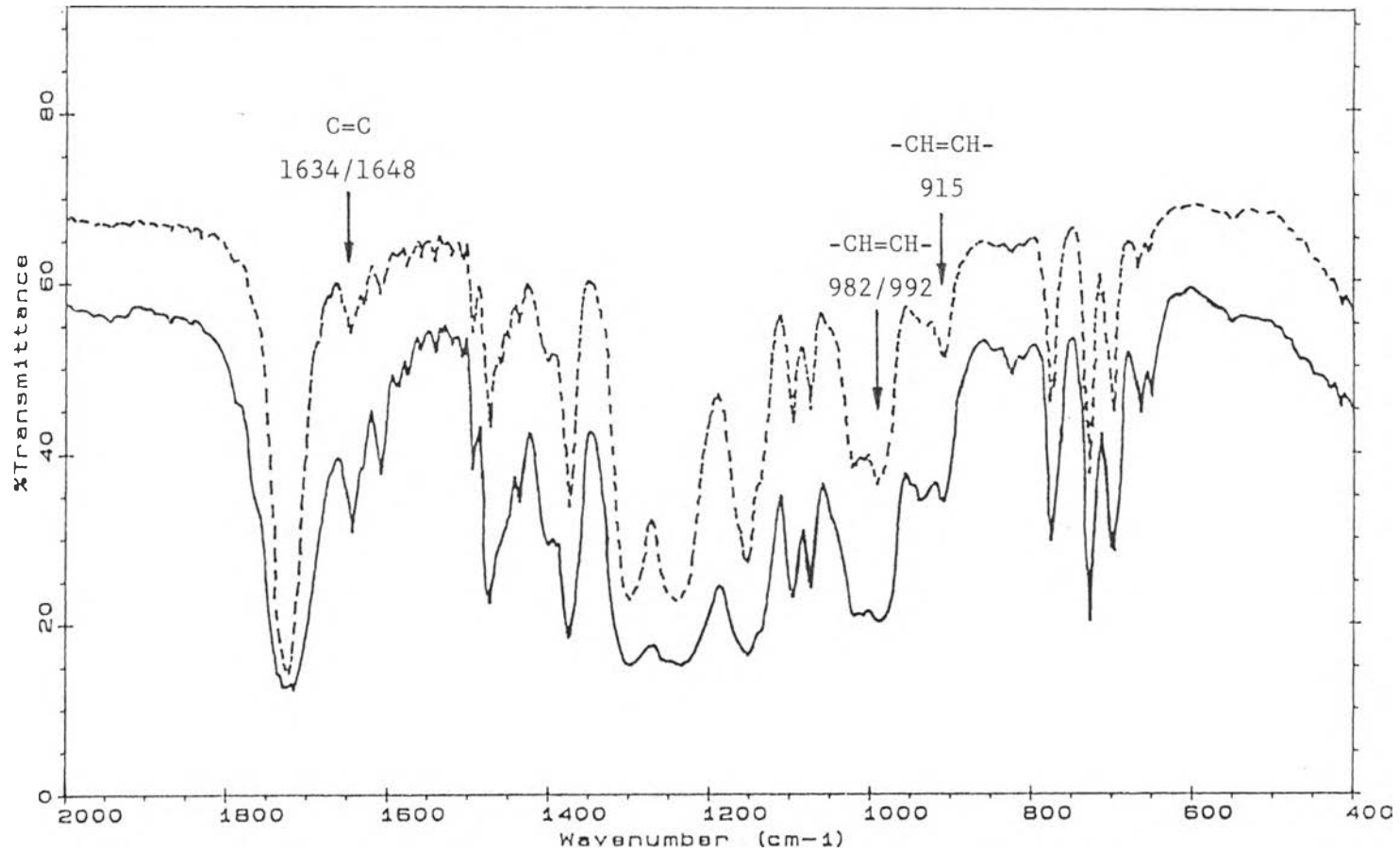


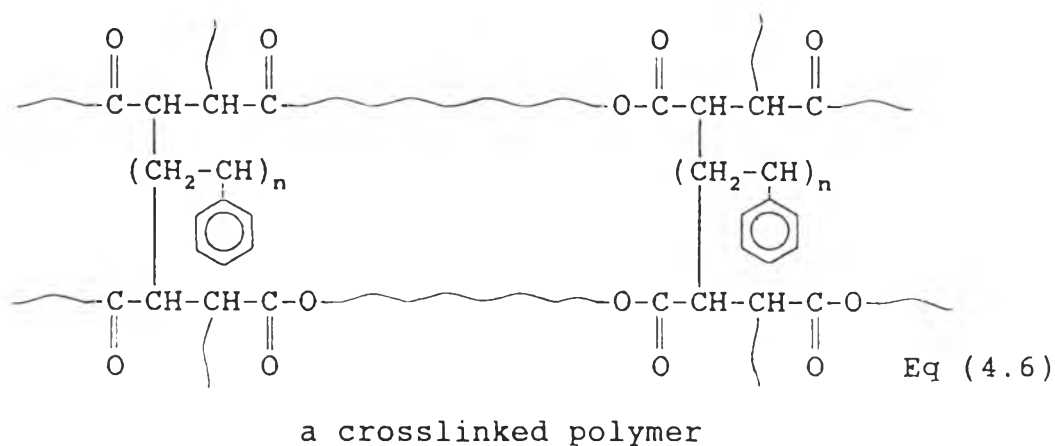
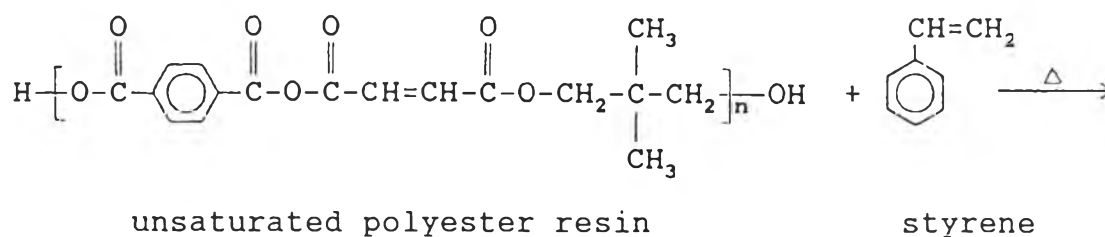
Figure 4.10 The infrared spectra of the polyester resins mixed with 1 phr of the BPO catalyst before the curing reaction and after the curing reaction at 150°C for 2 minutes. (----- before curing, ——— after curing.)

characteristic bands of the double bond of the unsaturated polyester resin and styrene. This is due to that the double bond is converted into a single bond during the curing reaction in the presence of the catalysts.

The unsaturated polyester resins used in this research are the reaction products of isophthalic acid, a dibasic aromatic acid, and neopentyl glycol, a dibasic aliphatic alcohol, in conjunction with maleic anhydride (15). Maleic anhydride provides an unsaturated or a reactive site. The active components present in the unsaturated polyester resin are usually ready for a molding compound. It is also known that during the preparation of the unsaturated polyester there is an isomerization process by which the maleic anhydride can be converted to the cis-configuration, the fumarate form. The fumarate form is usually more reactive than the maleate form in a free radical polymerization. In general, it is accepted that both the fumarate and the maleate forms are present in the unsaturated polyester chain.

In unsaturated polyester, the total amount of unsaturation includes the carbon to carbon double bonds in the polyester backbone, the maleate/fumarate, and those in the crosslinking monomer, the styrene. Thus, the heat of polymerization for unsaturated polyester including the conversion of the double bond functionalities into single bonds of the final rigid network is shown in Eq.4.6. It is

generally accepted that the styrene is incorporated in the cured polyester as a covalently bonded bridge between two polyester reactive sites. This bridge includes a distribution of styrene oligomer between two fumarate unsaturations. Notice that styrene is bifunctional and a network can only be formed if there are two or more reactive double bonds on the polyester backbone (13).



From the results in Figures 4.8-4.10, the probable chemical reaction due to thermal polymerization is crosslinking reaction of the unsaturations of the polyester resin. The change in the absorption intensity for the 1648-1634  $\text{cm}^{-1}$ , 985  $\text{cm}^{-1}$ , and 915  $\text{cm}^{-1}$  band, after 2 minute of the curing time, would be an indicator of the residual C=C group, including the pendent C=C groups, on the polymer

network structure. However, the curing reaction was still the phenomenon of the polymerization reaction, it is also dependent on time, temperature, and concentration of reactants. These preliminary results are regarded as a basic guideline for the control in processing of a certain type of curable resin.

#### 4.2.2 The Effect of Curing Time on the Extent of Reaction at the Middle Layer of the SMC

In this study, the curing time in the mold of the SMC was varied from 1 minute to 2 minutes while the amount of the catalyst in the SMC was constant. The processed material of the SMC at the middle layer was subjected to FTIR measurement of which the spectra were illustrated in Figures 4.11-4.13.

Figures 4.11-4.13 show the comparative spectra of the materials of the SMC at the middle layer which have a storage time of 30 days and a curing time in the mold at 150°C of 1 minute and 2 minutes, in the presence of the 2 phr TBPB, 2 phr DTBC, and 1 phr BPO catalysts, respectively. Increasing the curing time to 2 minutes, the intensity of the band at 915  $\text{cm}^{-1}$  decreased significantly, yet it still indicated of the residual of double bonds, or an incomplete polymerization, at the middle layer due to the presence of a considerable amount of the 915  $\text{cm}^{-1}$  band. Practically, it must be secure that a complete

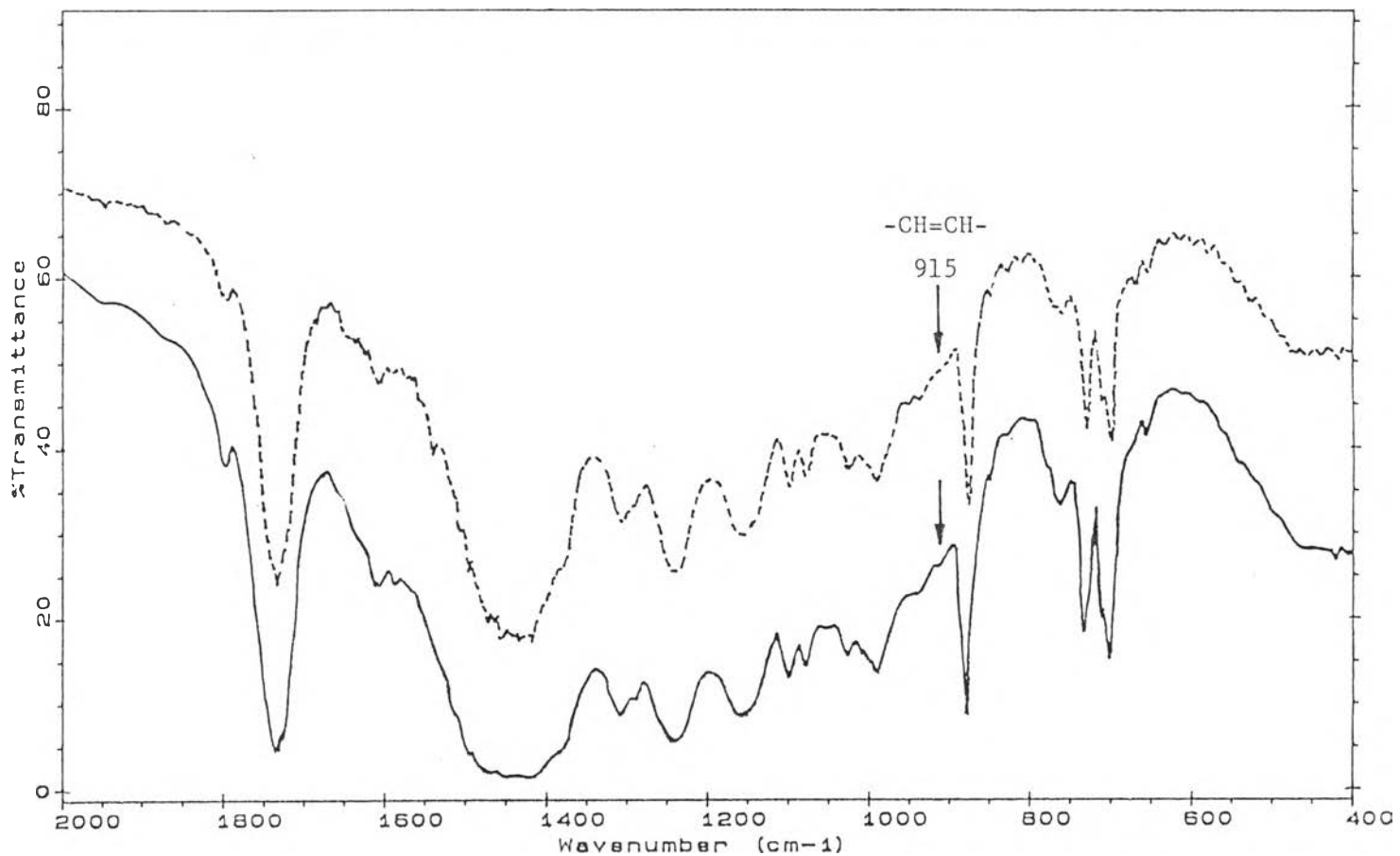


Figure 4.11 The infrared spectra of the SMC material, collected at the middle layer of the specimen, in the presence of the 2 phr TBPB catalyst.

(— after 1 minute curing at 150°C, ---- after 2 minutes curing at 150°C.)



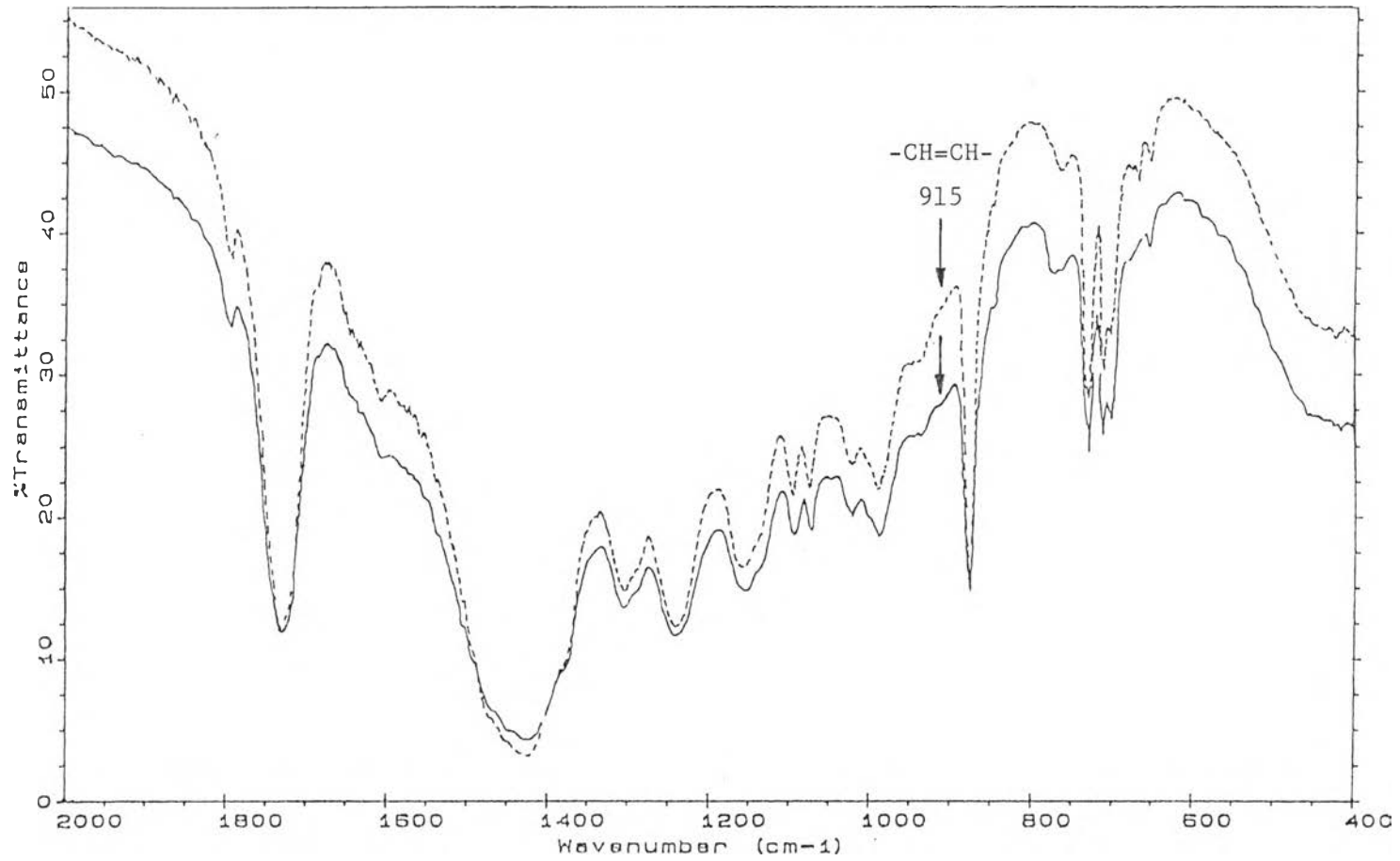


Figure 4.12 The infrared spectra of the SMC material, collected at the middle layer of the specimen, in the presence of the 2 phr DTBC catalyst.  
 (— after 1 minute curing at 150°C, ---- after 2 minutes curing at 150°C.)

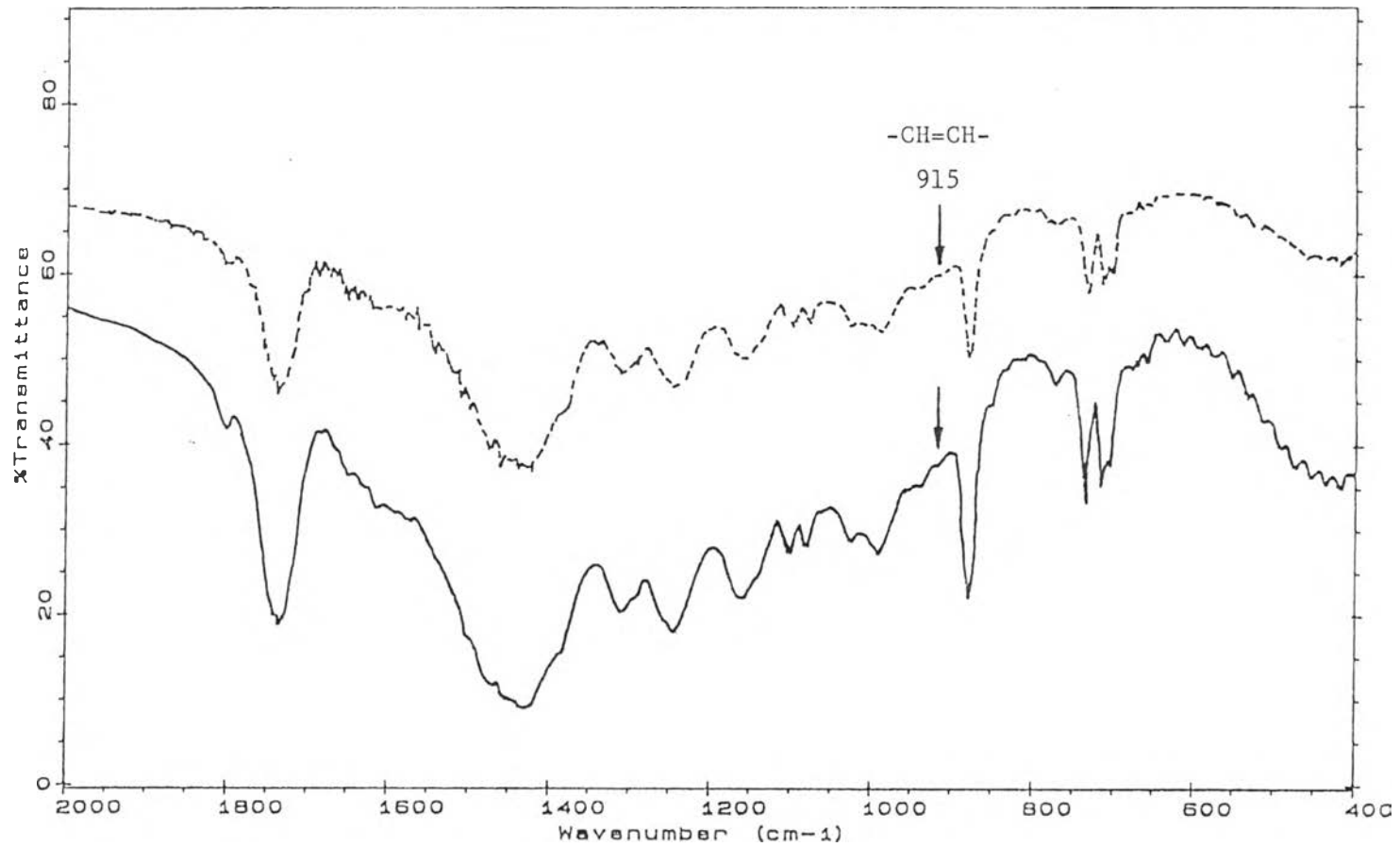


Figure 4.13 The infrared spectra of the SMC material, collected at the middle layer of the specimen, in the presence of the 1 phr BPO catalyst.

(— after 1 minute curing at 120°C, ---- after 2 minutes curing at 120°C.)

polymerization of the entire resin should be acquired at a given curing time under the specific material requirement.

#### 4.3 Effect of the Catalysts on Viscosity Characteristics on the Resin Paste

It is known that, by addition of relatively small amounts of an oxide or hydroxide of metals such as MgO (thickening agent), an appropriate polyester resin undergoes a thickening process, by which the system viscosity increases up to a semisolid state in a time of a few or several hours (20). This reaction is referred to as the thickening reaction and is the basis of the process employed to form SMC, since the resulting tack-free, easily handled compounds are still able to undergo a free radical curing while molding. A stable molding viscosity must be reached as soon as possible; after an induction time when the viscosity is low enough to allow fillers and glass fibers to wet out. The control of the viscosity increases is therefore necessary to perform a complete wet out and to enable molding at the right moments, and to obtain materials with good mechanical properties and good surface appeal. However, this control is difficult to achieve since small variations of factors such as a thickener concentration, bring about considerable changes in viscosity. These changes are not well understood, because an absolutely reliable reaction mechanism has not yet been established.

The important parameters of the thickening process were shown to be the molar ratio of metal oxide-to-carboxyl end groups, and the molecular weight of the resin (21).

Regarding the reaction mechanism itself, two theories have been put forward:

Vancso-Szmercsanyi et. al. (22) proposed a mechanism involving a two-step reaction between carboxyl end groups and metal oxide, with an initial formation of basic or neutral salts, followed by the complexation of these salts by the ester groups in the chains and/or the hydroxyl end groups as shown in Figure 4.14. This "complexation reticulation" could explain the increase in viscosity:

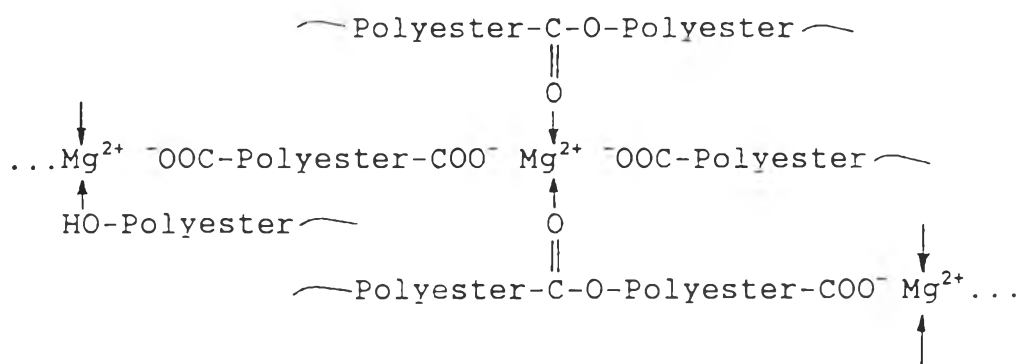
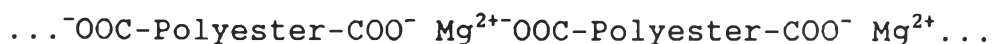


Figure 4.14 The complexation reticulation of MgO and polyester resin.

Burns and Gandhi, and more recently Gruskiewicz and Collister (23), described the thickening reaction as the formation of a polymeric neutral salt:



Eq (4.7)

If a sufficient amount of  $\omega,\omega'$ -dicarboxy chains is present, the ionic polymer formed is long enough to exhibit an entanglement coupling, thus increasing the viscosity.

In this study, the paste of magnesium oxide plays a vital role in viscosity behavior of the resin mix. When 3 phr of magnesium oxide was incorporated into the resin mix, the viscosity measured after 2 hour mixing was extremely high. This behavior obstructed the effect of the catalysts under study which was due to the rapid increase in viscosity in a very short time. It is probably wise to reduce the concentration of magnesium oxide to 1.2 phr so that all the desired properties can be investigated. Figure 4.15 depicts the effect of the concentration of magnesium oxide on viscosity of the resin paste.

Figure 4.15 shows that the major contribution of a viscosity increase is totally due to the presence of magnesium oxide. The presence of the catalyst could only increase the viscosity to an insignificant level. As already described earlier, the TBPB catalyst can only start the curing reaction which causes the slow increase in viscosity. It is interesting to point out that the increase in paste viscosity due to the presence of magnesium oxide is a time dependent phenomenon. It is

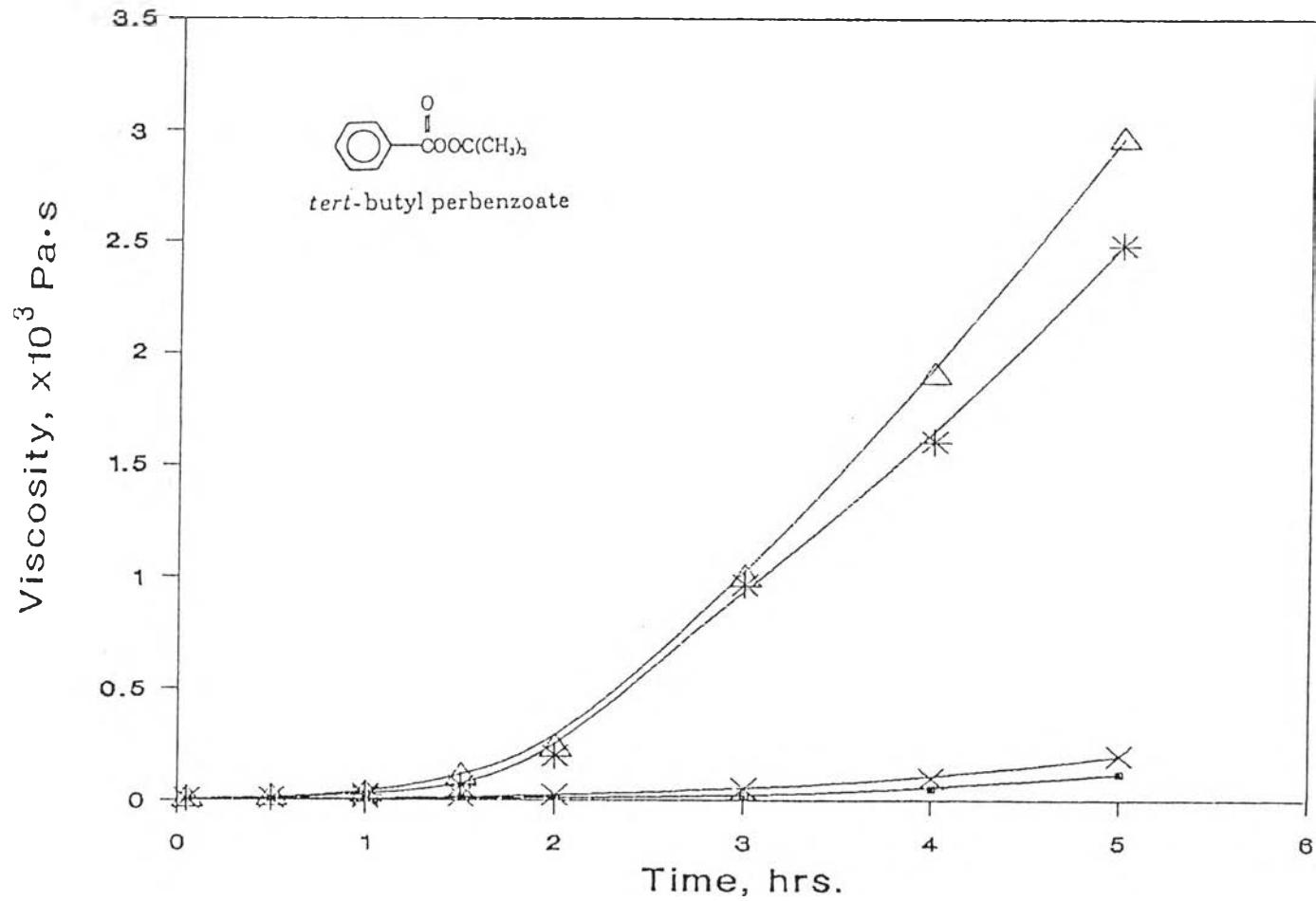


Figure 4.15 Effect of the concentration of MgO on the paste viscosity under the influence of the TBPB catalyst. ( —●— MgO 1.2 phr; —×— MgO 1.2 phr, TBPB 2 phr; —\*— MgO 3 phr; —△— MgO 3 phr, TBPB 2 phr.)

suggested that magnesium oxide can build up a physical structure to the resin known rheologically as a "permanent thixotropic behavior". The same phenomenon was observed in Figure 4.16.

Similar results were obtained with other catalysts previously used, the results of these catalysts were showed in Figures 4.17 and 4.18. Of these three catalysts in conjunction with the fixed amount of magnesium oxide, the most effective catalysts in producing a high viscosity is the BPO, followed by the DTBC and the TBPB. With this series of result in terms of effectiveness in viscosity, an appropriate amount of the catalyst to produce a desirable viscosity can be tailor made.

Theoretically, the type and concentration of the catalyst influence greatly the paste viscosity, which in turn, affects the extent of wetting of glass fibers through impregnation. The useful viscosity range to obtain a good impregnation is in the order of 3 to 30 Pa-s. Too low a paste viscosity would make a poor dispersion to the glass fibers. By such, the glass fibers could not be well dispersed in the SMC sheet from which poor mechanical properties occurred. Too high a paste viscosity imposed difficulties to the paste impregnation into glass fibers. Then the wetting of the glass fibers by the paste would not take place and hence an even poorer dispersion was the next consequence, followed by an failure of this material under

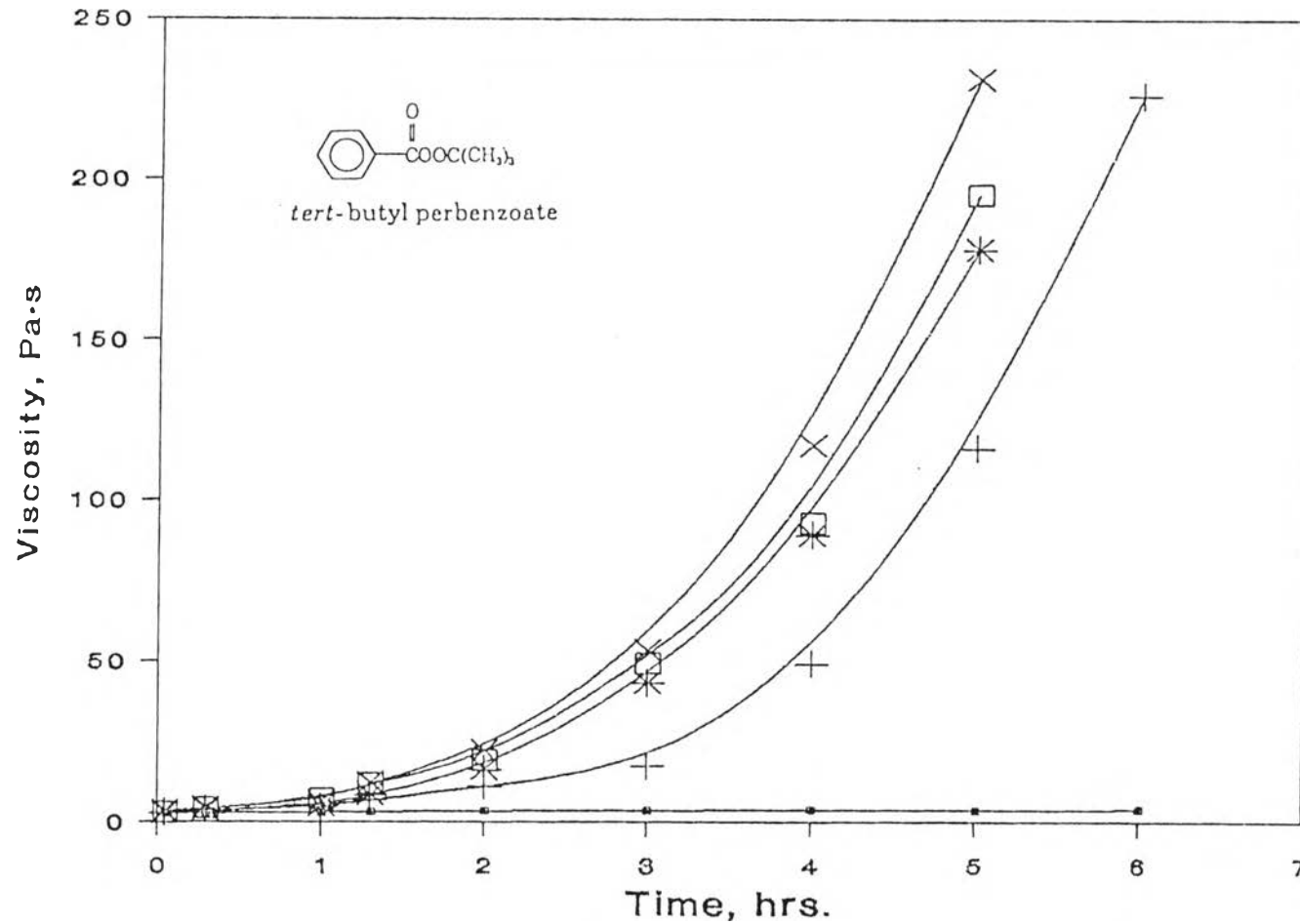


Figure 4.16 Effect of the concentration of TBPB catalyst on the paste viscosity under the influence of 1.2 phr MgO and in the absence of MgO. (TBPB concentrations: —+— 0 phr, —\*— 1 phr, —□— 2 phr, —X— 3phr; —●— 2 phr and absence of MgO.)



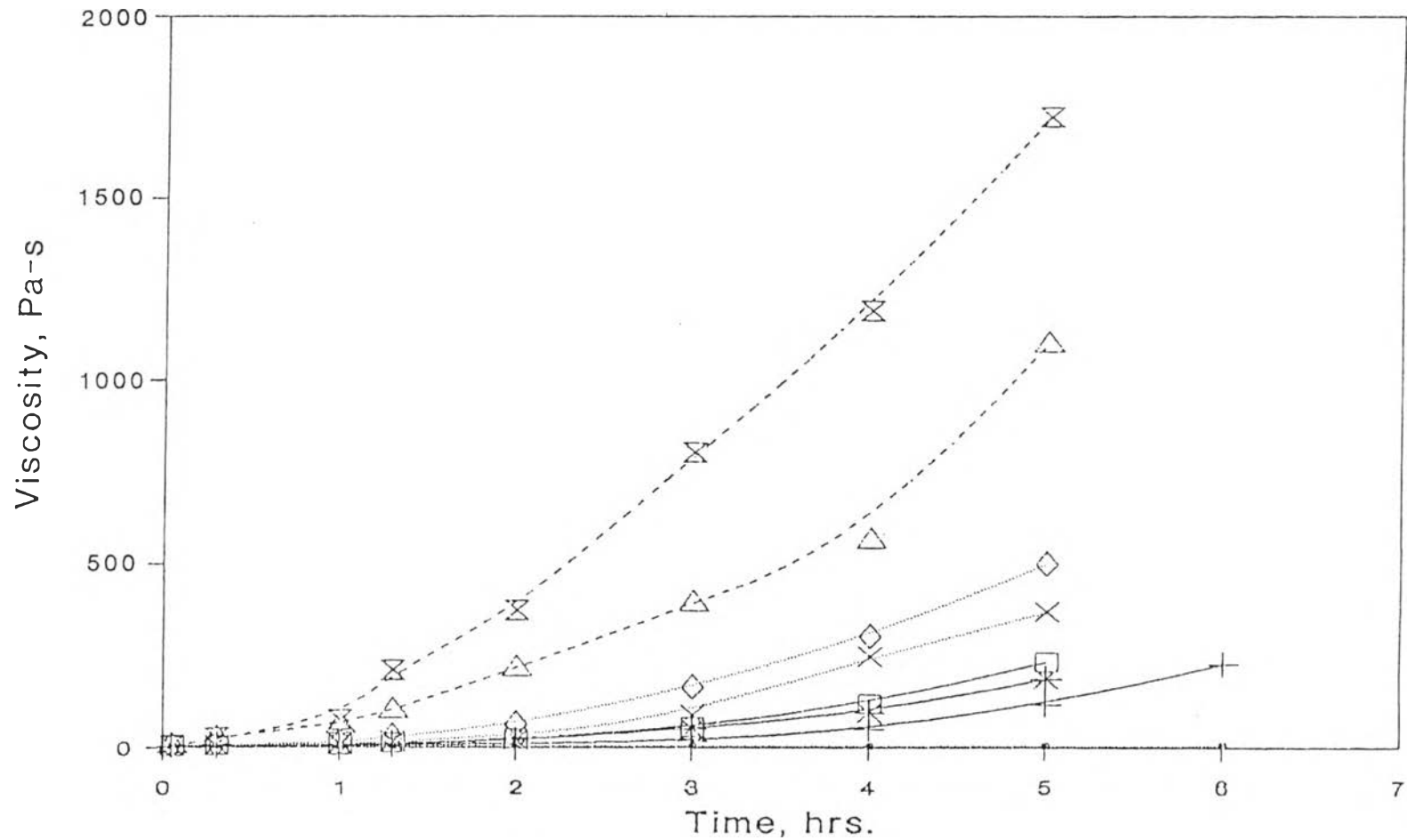


Figure 4.17 Effect of the catalysts on viscosity of the polyester paste after 5 hours of mixing.

( —•— MgO 0 phr; —+— Catalyst 0 phr; —\*— TBPB 2 phr, —□— TBPB 3 phr;  
 —×— DTBC 1 phr, —◇— DTBC 2 phr; —△— BPO 0.5 phr, —⊗— BPO 1 phr.)

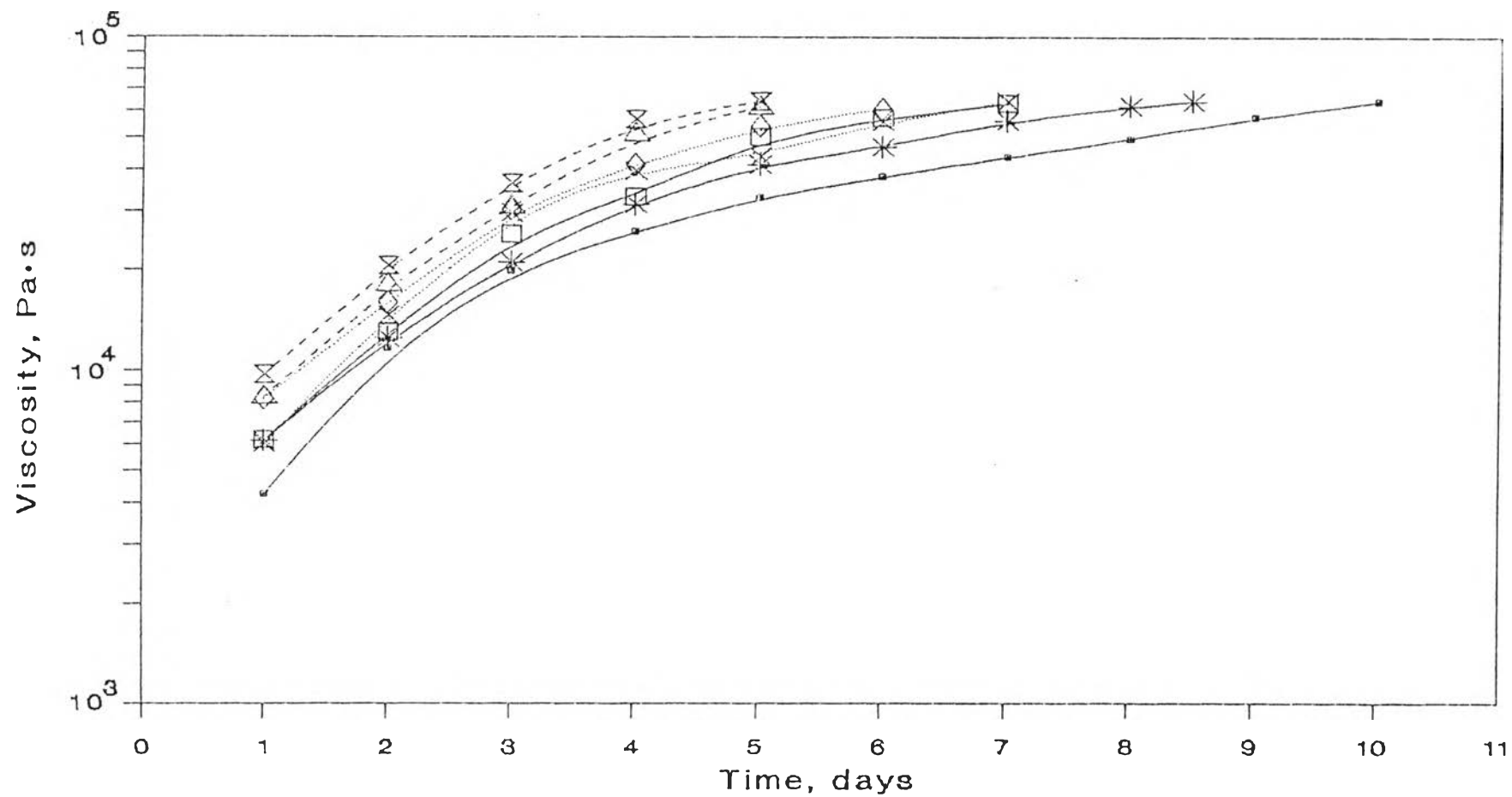


Figure 4.18 Effect of the catalysts on viscosity of the polyester paste after mixing for 1 day.

( —●— Catlyst 0 phr; —✱— TBPB 2 phr, —◻— TBPB 3 phr; —✕— DTBC 1 phr,  
 ◊— DTBC 2 phr; —△— BPO 0.5 phr, —⊠— BPO 1 phr.)

a service life.

As already described earlier on effects of the amount of catalysts on the paste viscosity, it seems that the extent of such an effect is of a secondary consideration as it depends, to a larger extent, on a time scale after thoroughly mixing with magnesium oxide. It was found that the 3 phr of magnesium oxide was the optimum concentration for this unsaturated system of polyester resin. Because this concentration gives a stable impregnation of glass fiber by the paste and provides consequently a rapid thickening reaction of the SMC within 5-6 hours. The sheet of SMC can also be kept at room temperature, instead in an oven with a temperature higher than room temperature in order to speed up the completely thickening reaction of the SMC.

#### 4.4 Effect of the Catalysts on Storage Life of the SMC

Studying the effect of catalysts on storage life of the SMC was done with a Shore durometer (type A) which measured the hardness of the SMC surface resulting from the thickening reaction of magnesium oxide and the catalyst.

Since the unsaturated polyester resin can undergo thermal polymerization at ambient temperature, even in the absence of catalysts. This reaction will premature the resin which makes it a waste. It is of great interest to

investigate this effect and thus a storage time can be assessed.

#### 4.4.1 Effect of Temperature on Storage Life of the SMC in the Absence of the Catalyst

In the presence of magnesium oxide, the thickening reaction of the polyester resin is accelerated which can be measured in terms of the paste viscosity and the hardness of the SMC before curing. The thickening reaction usually increases with an increase in temperature due to thermal polymerization. The effect of a storage time on hardness of the SMC at 28°C and 40°C is showed in Figure 4.19. It is found that the higher the temperature, the greater the hardness of the SMC. Likewise, the longer the storage time, the harder the SMC. At higher temperatures, there is a larger amount of thermal energy to accelerate the thickening reaction of MgO in the unsaturated polyester.

Storing the SMC at a high temperature environment, the SMC hardness increases significantly. At high temperatures, the molecules of MgO can thicken the polyester resin rapidly. In conjunction with the catalysts, the higher temperatures accelerate the catalyst decomposition rate and thereby an increase in hardness is observed due to the rapid curing and crosslink reaction as to be described in the next section.

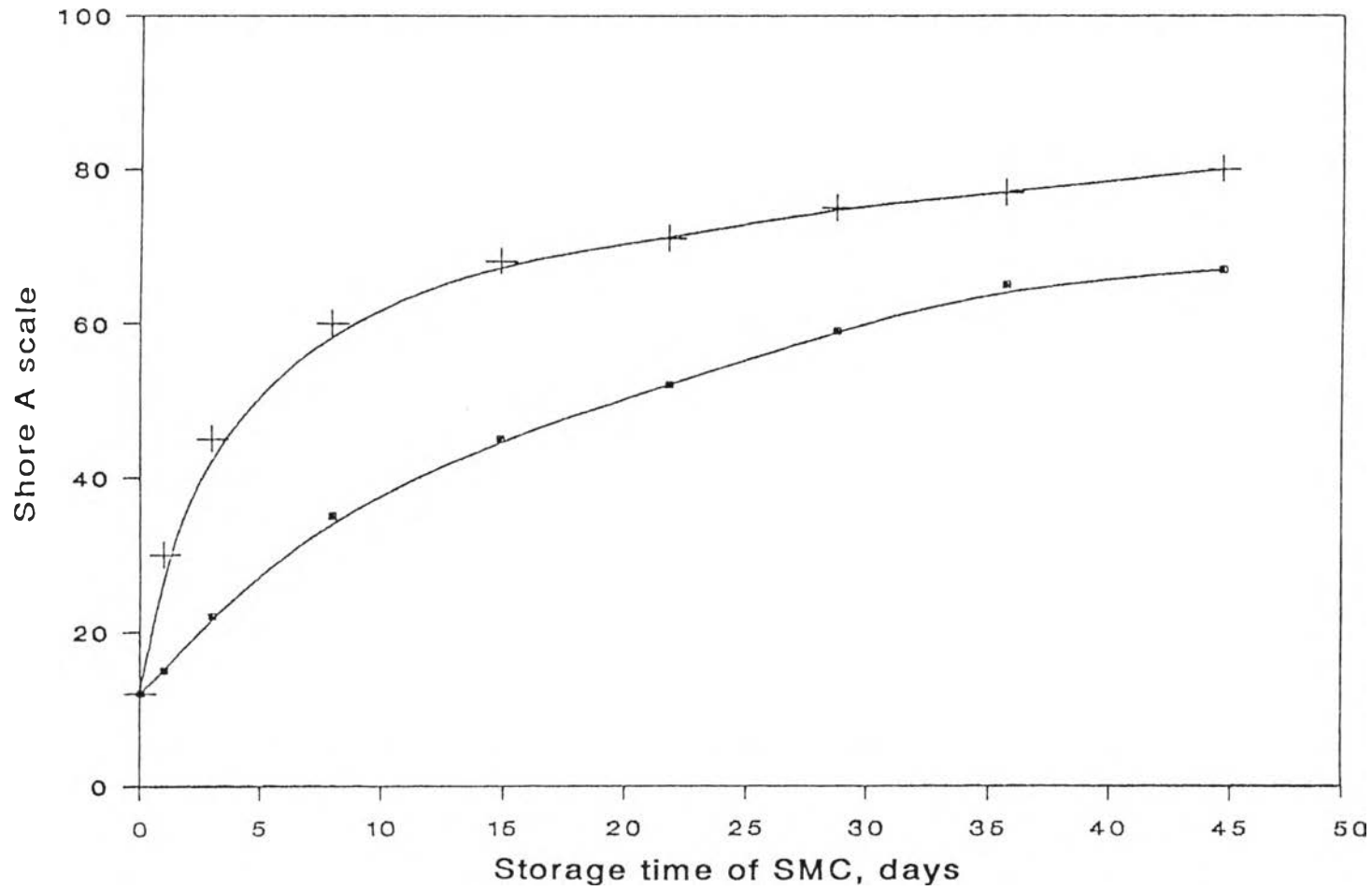


Figure 4.19 Effect of storage life on hardness of the SMC at the temperatures of 28°C and 40°C in the absence of the catalysts. ( —■— 28°C, —+— 40°C.)

#### 4.4.2 Effect of the Type and Concentration of the Catalysts on Storage Life of the SMC

According to the formulation set in Table 3.7 and the assessment of premature of the SMC by the durometer, it was inevitable that the types and concentration of the catalysts imposed quite a significant effect on storage life of the SMC. Figures 4.20-4.22 show the detailed results of the TBPB, DTBC, and BPO catalysts.

The thickening reaction of MgO with respect to time and the rate of crosslink reaction are the attribute to the extent of hardness of the SMC. Both above mentioned are directly controlled by the decomposition temperature at half life of the catalyst. Basically, the lower the decomposition temperature, the faster the hardening of the SMC. A good example is the case of the BPO catalyst, i.e, the half-life temperature of the catalyst is 73°C which is lower than those of the DTBC and TBPB catalysts. Therefore, the storage life of the SMC containing the BPO catalyst will usually be shorter and the processing is consequently much more difficult due to the flow ability in the mold during molding. In addition, it was found that styrene monomer incorporating in the SMC could normally volatile and undergo thermal polymerization or dark reaction. It is suggested from the experiment that the appropriate hardness of the SMC for

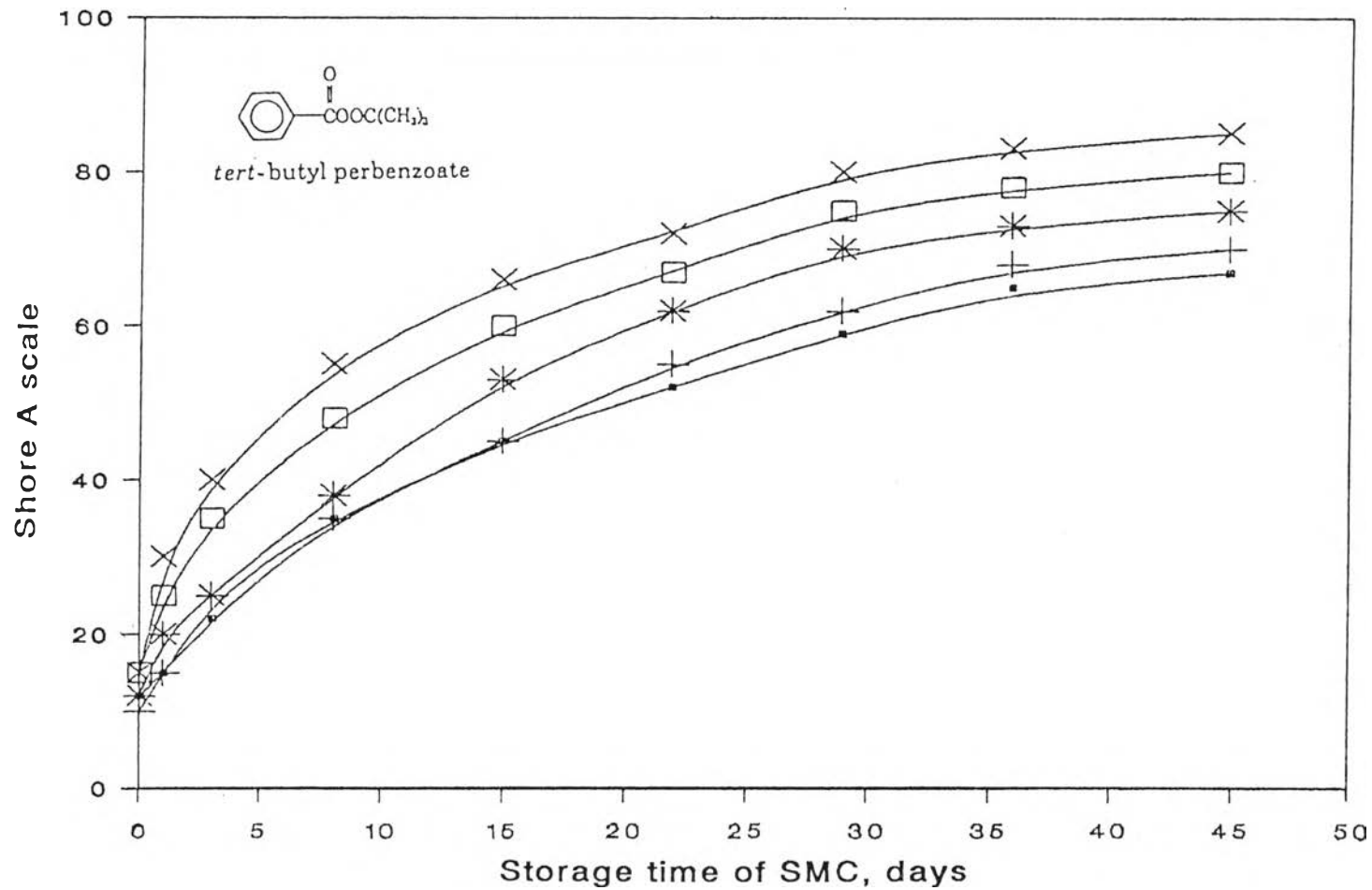


Figure 4.20 Relationship between the storage life and hardness of the SMC in the absence/ presence of the TBPB catalyst at the concentrations of 0.5, 1, 2, and 3 phr. (—•— 0 phr, —+— 0.5 phr, —\*— 1.0 phr, —□— 2.0 phr, —X— 3.0 phr.)

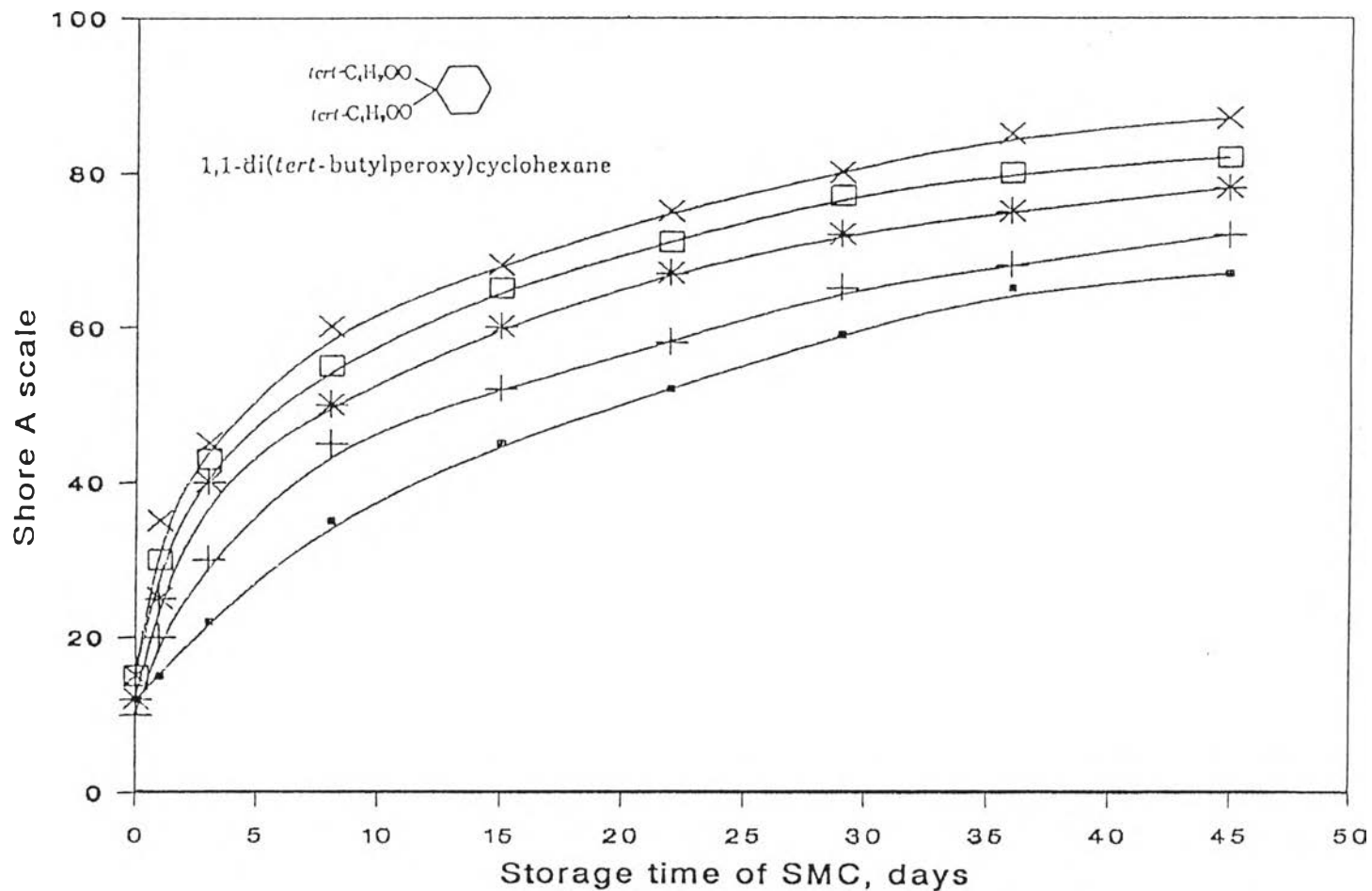


Figure 4.21 Relationship between the storage life and hardness of the SMC in the absence/presence of the DTBC catalyst at the concentrations of 0.5, 1, 2, and 3 phr. (—■— 0 phr, —+— 0.5 phr, —\*— 1.0 phr, —□— 2.0 phr, —X— 3.0 phr.)



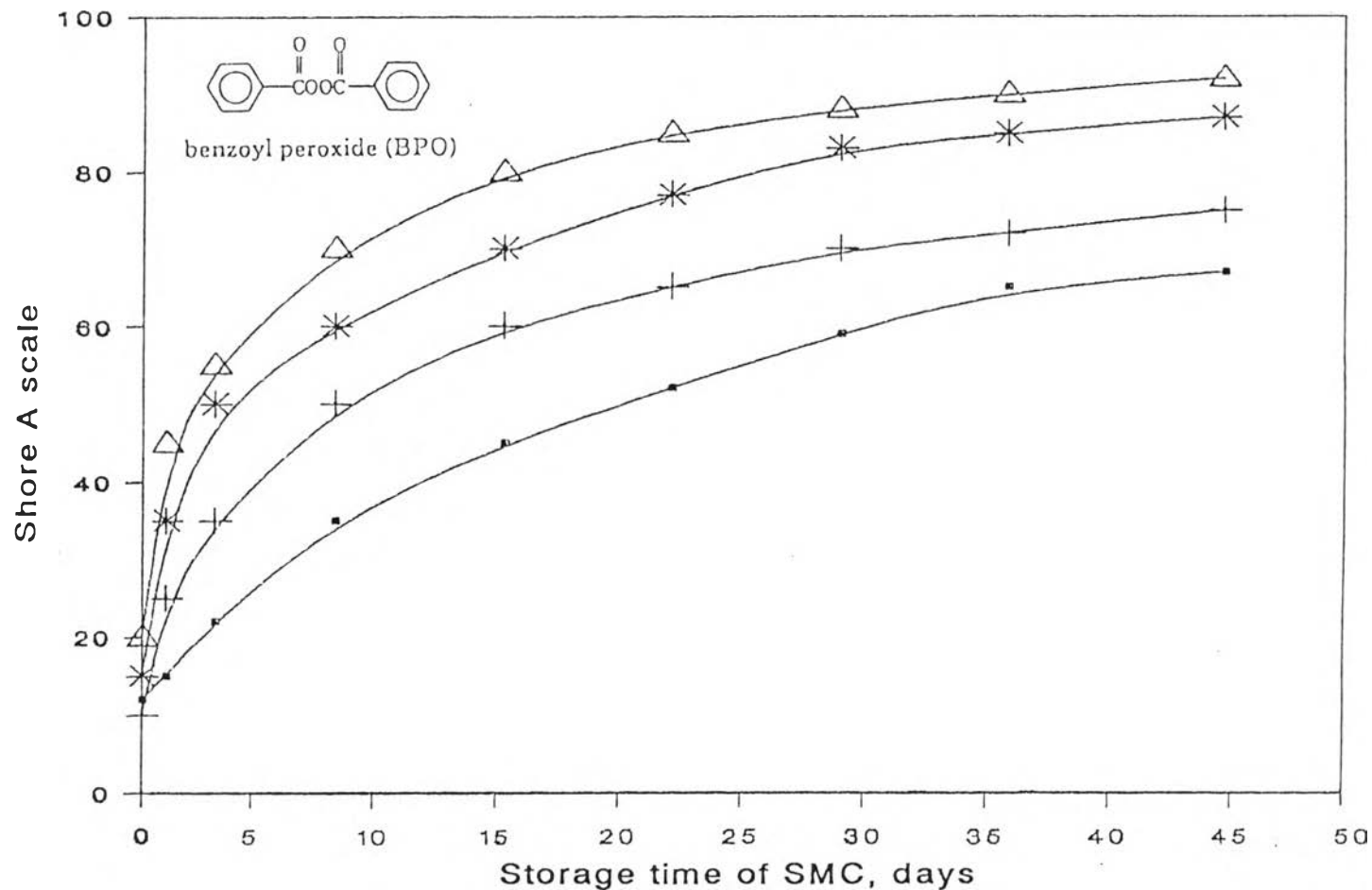


Figure 4.22 Relationship between the storage life and hardness of the SMC in the absence/ presence of the BPO catalyst at the concentrations of 0.05, 0.1, and 1 phr. (—●— 0 phr, —+— 0.05 phr, —\*— 0.1 phr, —△— 1.0 phr.)

an ease and economical fabrication should be of 60 units of the Shore A scale.

#### 4.5 Effect of the Catalysts on Mechanical Properties of the SMC

The duration of the curing step depends on how long it takes for the material to reach a critical conversion level, at which it is dimensionally stable and thus can be removed from the mold without losing its shape or blemishing its surface. To minimize the high level of confidence of the conversion, throughout the mold should be opened as soon as the overall conversion in the mold was above the critical value. However, the conversion cannot be measured directly, thus the end of the cure must be predicted by means of indirect measurements which can functionally relate to cure (24).

In this study, test specimens were prepared from the formulation in Table 3.7 and subjected to the test methods of ASTM D790 (20) mentioned previously. The flexural test was used as a method to follow up the effect of cure time on mechanical property of the SMC, influenced by the catalysts: the TBPB, DTBC, BPO, additions of PBQ to the catalysts, and the dual catalysts.

#### 4.5.1 Effect of the TBPB Catalyst on Mechanical Properties of the SMC

The TBPB was a wellknown catalyst used in the SMC at present time. It has a half-life temperature in 10 hours at 104°C. The forming temperature of SMC in the mold was 150°C. The effects of the TBPB catalyst of 2 phr on mechanical strength expressed as flexural strength and modulus and storage time were shown in Figures 4.23-4.24, respectively. However, there are available data to compare the mechanical properties between the results from the experiments and the calculated ones from equations 3.1 and 3.2. A standard deviation analysis was run on the results of the four specimens as shown in Appendix B.

Figures 4.23-4.24 show the comparative flexural strength and modulus of the SMC when the curing time in the mold of the SMC was varied from 1, 2, and 3 minutes. From the results, the mechanical property of the SMC depended greatly on the curing time in the mold. The flexural strength and modulus were found to be lower for 1 minute of curing time at all levels of storage time. The flexural strength and modulus were almost equal at the levels of curing time for 2 and 3 minutes.

Based on the characteristic peaks of the cured products on a FTIR spectra, there existed a few residues of the uncured C=C groups in the SMC with 1 minute

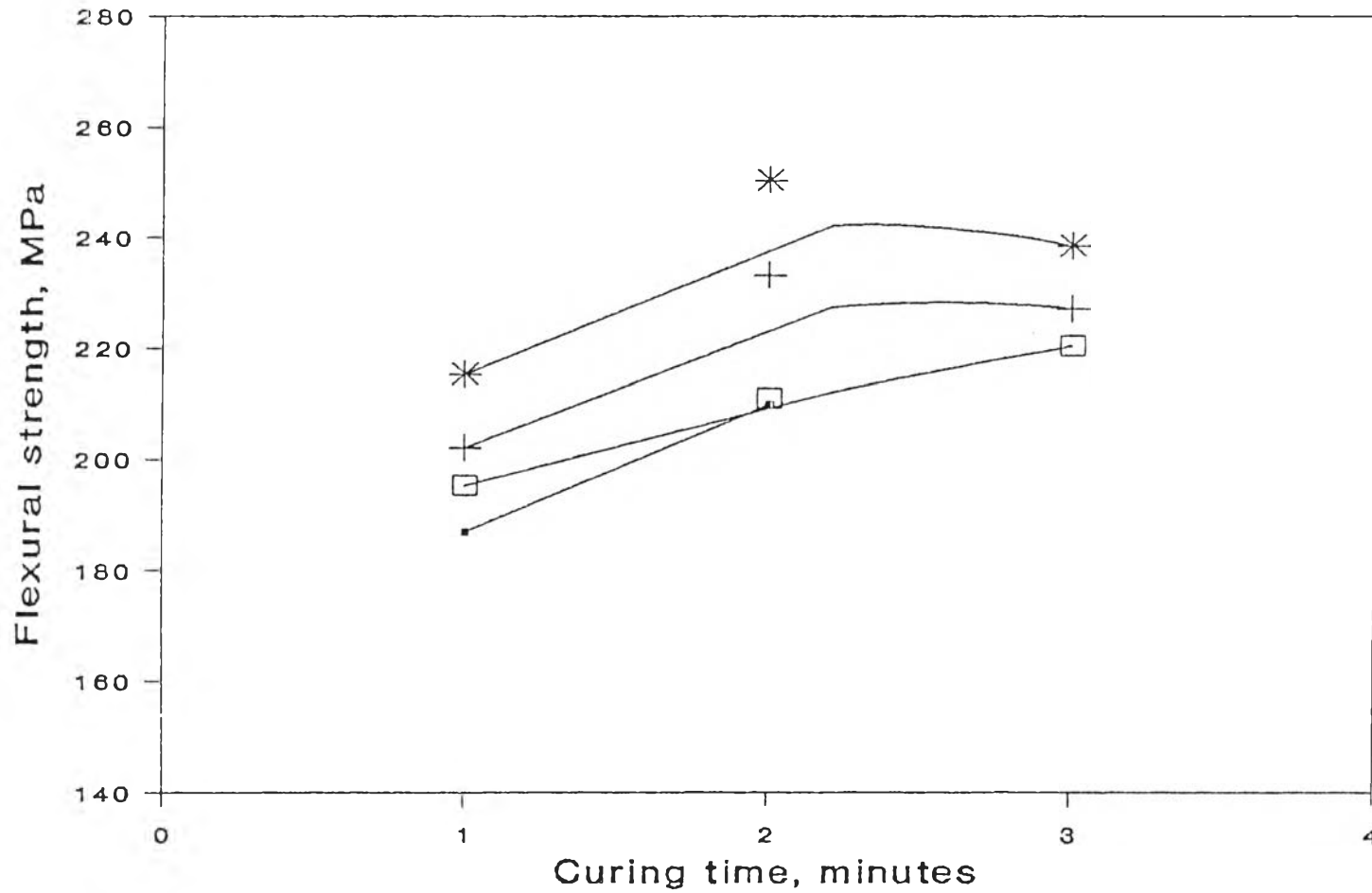


Figure 4.23 Effect of curing time on flexural strength at a function of storage times.  
 (2 phr of the TBPB catalyst; —■— 3, —+— 17, —\*— 30, —□— 45 days of storage.)

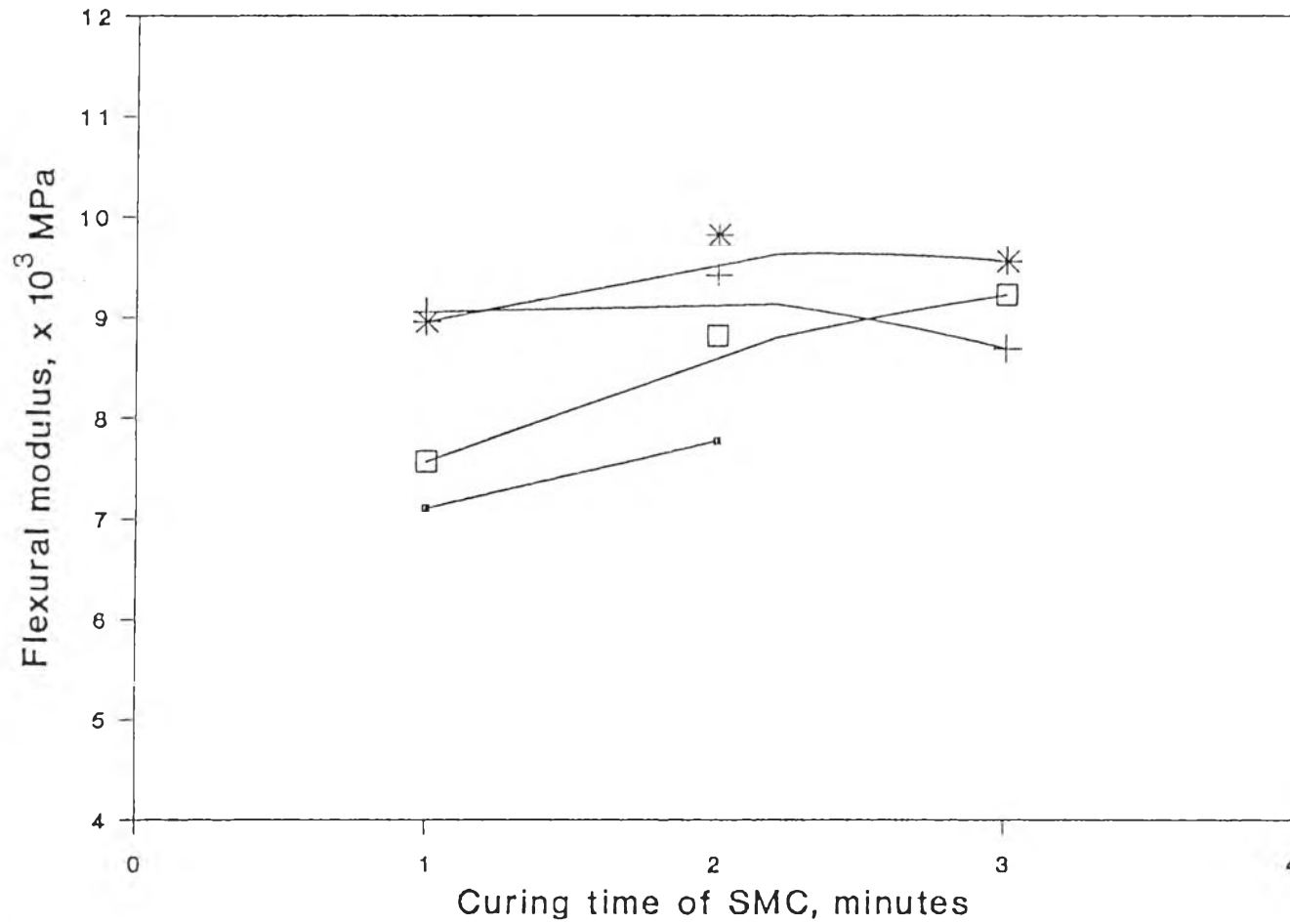


Figure 4.24 Effect of curing time on flexural modulus at a function of storage times.  
 (2 phr of the TBPB catalyst; —■— 3, —+— 17, —\*— 30, —□— 45 days of storage.)

of curing time. It showed that a 1 minute of curing time might not be enough for complete curing of the SMC. By such an indication, the product could not completely crosslink which resulted in low mechanical strength of the SMC.

From the results in Figures 4.23-4.24, the flexural strength and modulus of the SMC which has a storage time of 45 days, was lower than those of 17 and 30 days. These results showed that the appropriate storage time, or shelf life, of the SMC at the room temperature (28°C) should not be longer than 30-45 days. Because of the longer the storage time, the higher viscosity; the SMC sheet, then, becomes too hard to be indented on the surface. The SMC was too viscous to flow in the molding process.

The shelf life and working life are terms related to and dependent upon the gel time of a thermosetting system. The working life is the time available for processing the system from the point the reactants are first brought together. Only under very unusual conditions does the working life equal or exceed the gel time.

The shelf life represents the length of storage time during which the SMC will remain stable (i.e., the time available for storing the material before processing begins). One-can system is designed to provide

very long shelf lives at room temperature or below. The shelf life of the SMC can be influenced by other factors besides reaction kinetics. For example, contamination of the resin by moisture, CO<sub>2</sub>; or other airborne particulate can seriously affect the gelation characteristics of unsaturated polyester resins (25).

Regarding the concentration of the TBPB catalyst on the flexural strength and modulus of the SMC under the influence of the curing time at 1 and 2 minutes, the storage time of the SMC at 3, 17, and 30 days are presented in Figures 4.25-4.26. It showed that the SMC with the low concentration of TBPB catalyst at 0.5 phr had lower strength due to the effect of low concentration of the catalyst. The curing reaction of the SMC occurred slowly and was unable to complete the curing reaction within 1 or 2 minutes. Likewise the effect of catalyst concentrations at 2 and 3 phr on flexural strength and modulus of the SMC was not significantly enough to elaborate. Considering the effect of the storage time on the flexural strength and modulus of the SMC, it is found that 3 days of storage time created lower mechanical strength than those of 17 and 30 days; the effect of concentration of the TBPB catalyst at 1 to 3 phr on flexural strength and modulus of the SMC was not significantly different. The most influencing parameter on the mechanical properties of the SMC is the curing time in the mold, i.e., the longer the curing time, the greater the mechanical strength.

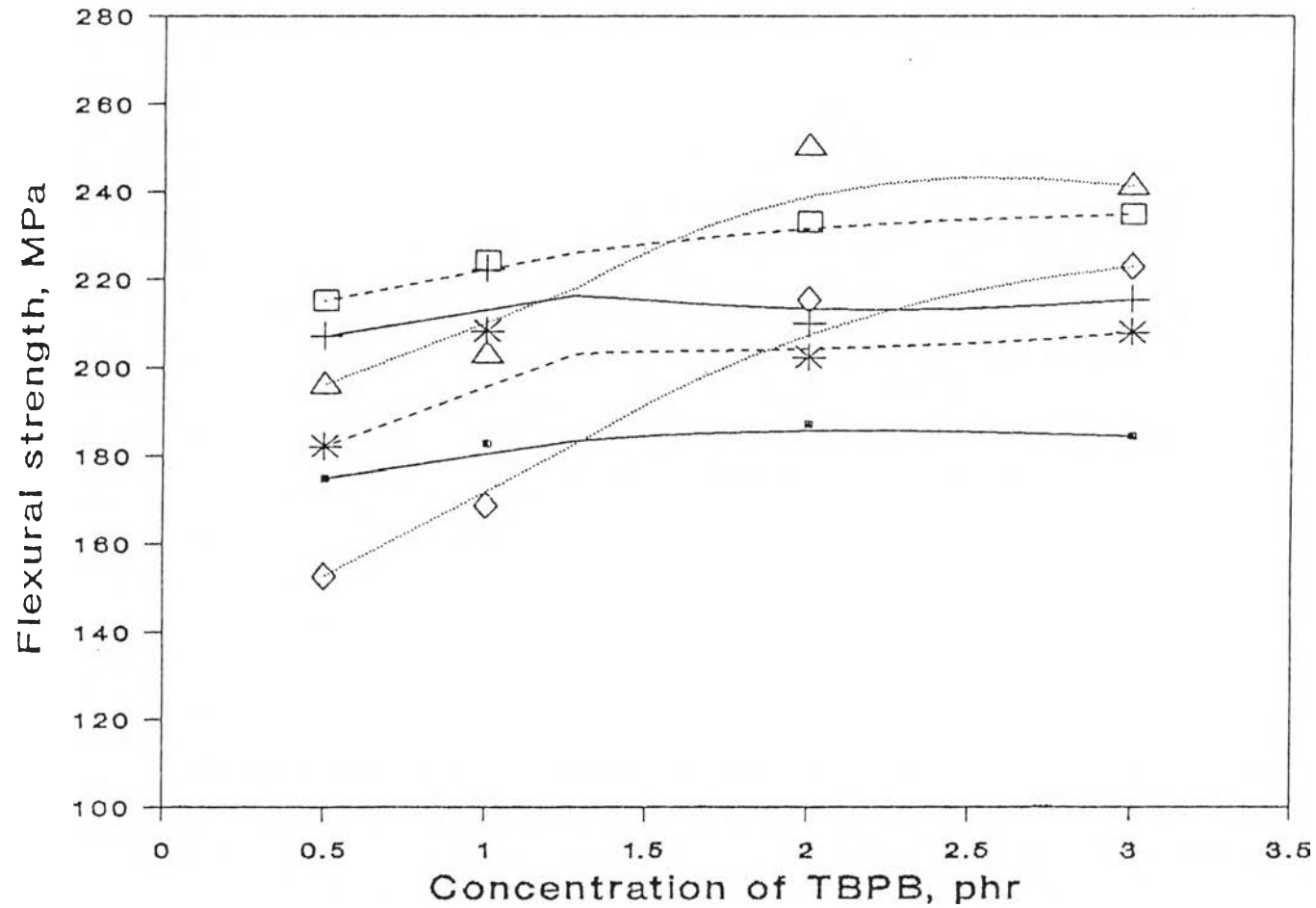


Figure 4.25 Effect of the concentrations of the TBPB catalyst on the flexural strength of the SMC under the influence of the storage time and the curing time. ( —●— 3 days, 1 min; —⊕— 3 days, 2 min; —\*— 17 days, 1 min; —□— 17 days, 2 min; —◇— 30 days, 1 min; —△— 30 days, 2 min.)



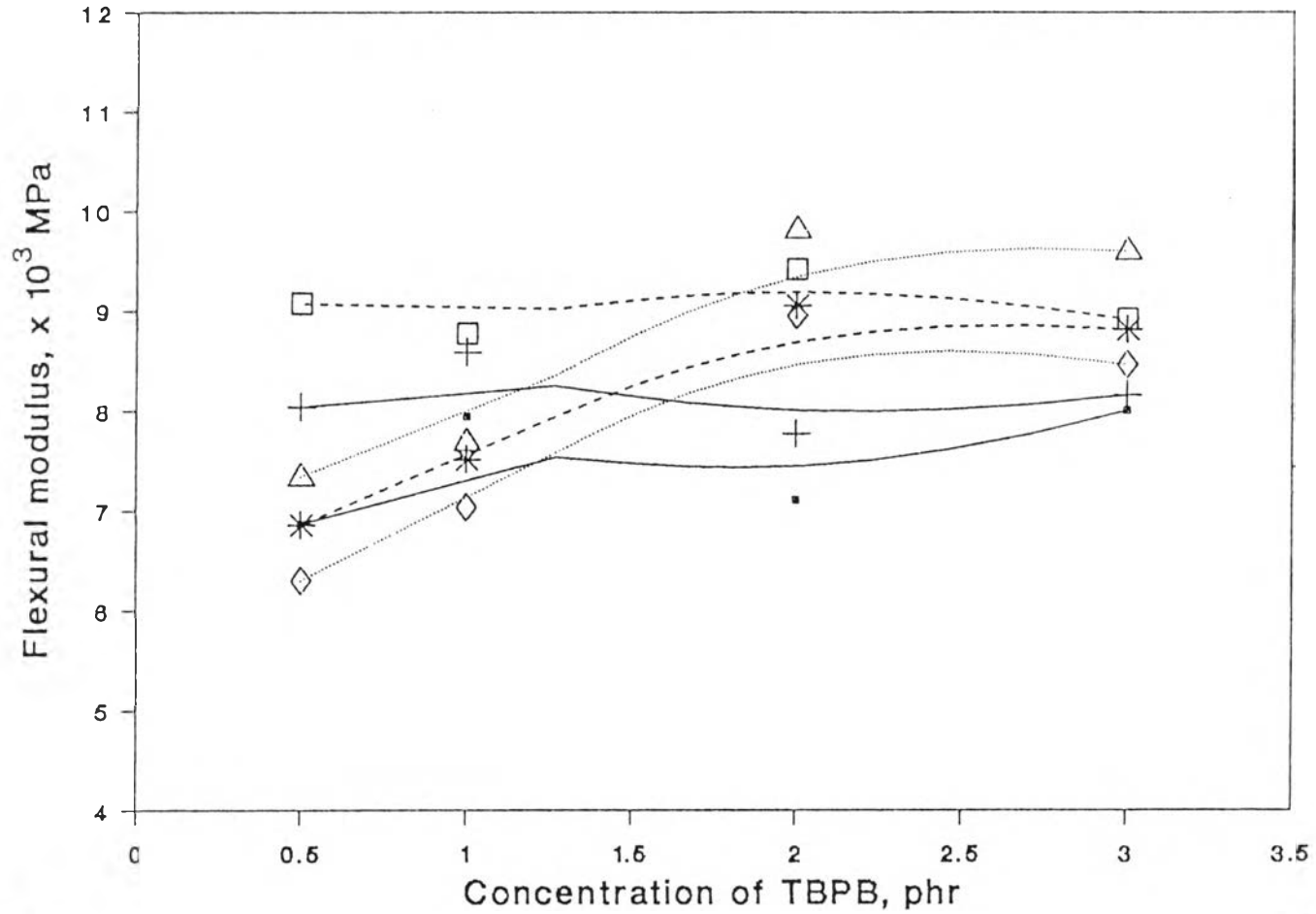


Figure 4.26 Effect of the concentrations of the TBPB catalyst on the flexural modulus of the SMC under the influence of the storage time and the curing time. ( —●— 3 days, 1 min; —+— 3 days, 2 min; —\*— 17 days, 1 min; —□— 17 days, 2 min; —◇— 30 days, 1 min; —△— 30 days, 2 min .)

#### 4.5.2 Effect of the DTBC Catalyst on Mechanical Properties of the SMC

The DTBC catalyst has a lower half-life temperature in 10 hours, at 93°C, than the TBPB catalyst. With such a property, it is useful in reducing the curing time of the SMC. On trial and error, a curing temperature at 150°C gave the fabricated products a normal appearance, i.e., they looked good and their strength was high.

Figures 4.27-4.28 illustrate the concentration effect of the DTBC catalyst on the flexural strength and modulus of the SMC under the same condition as that of the TBPB catalyst mentioned previously. It is found that the flexural strength and modulus of the SMC are highest at 1 phr of the DTBC, and the storage time of the SMC at 17 days, of which the hardness of the SMC was approximately 60-70 Shore A.

Figures 4.27-4.28 show the similar results as compared to the TBPB catalyst for the SMCs fabricated with cure times of 1 and 2 minutes. Again little difference was seen from the flexural strength and modulus of the 1 and 2 minutes curing times, indicating that the 1 minute cure time was not an optimum limit. The SMC cured for 1 minute had low mechanical strength due to insufficient cure time. This caused of delamination or blistering of SMC sheet. Referring to (1), the demold time was found to have

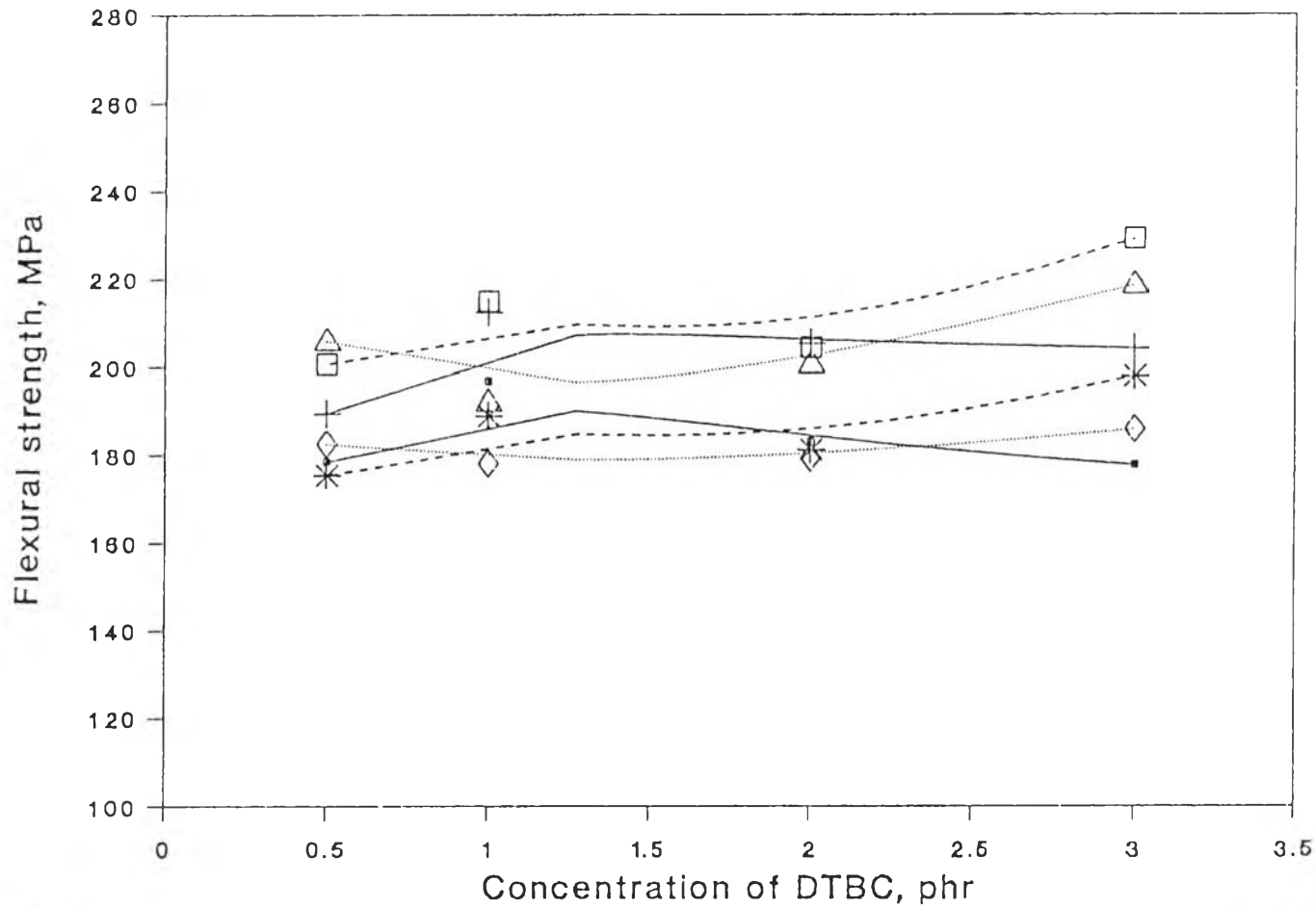


Figure 4.27 Effect of the concentrations of the DTBC catalyst on the flexural strength of the SMC under the influence of the storage time and the curing time. ( —●— 3 days, 1 min; —+— 3 days, 2 min; —\*— 17 days, 1 min; —□— 17 days, 2 min; —◇— 30 days, 1 min; —△— 30 days, 2 min.)

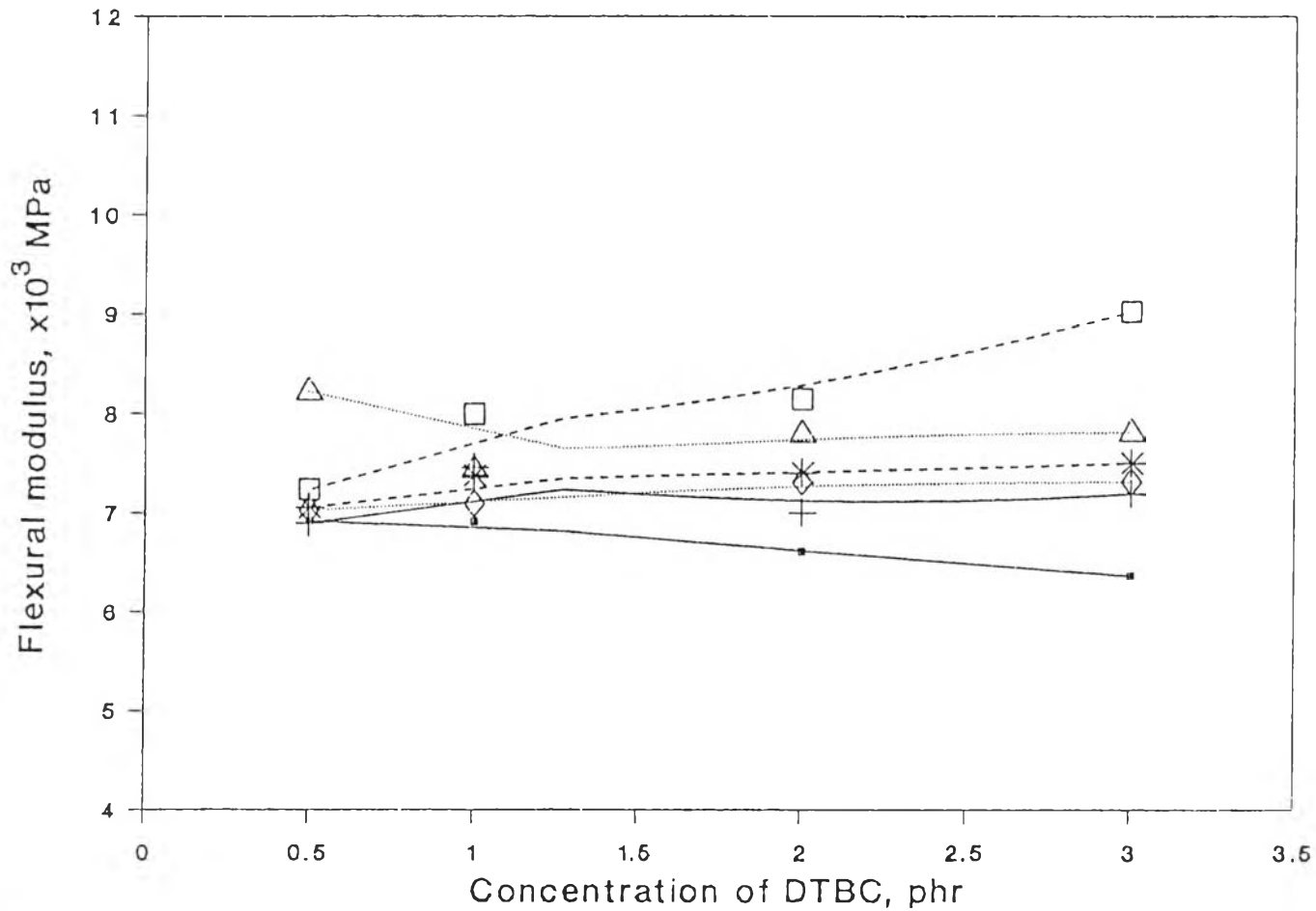


Figure 4.28 Effect of the concentrations of the DTBC catalyst on the flexural modulus of the SMC under the influence of the storage time and the curing time. ( —●— 3 days, 1 min; —+— 3 days, 2 min; —\*— 17 days, 1 min; —□— 17 days, 2 min; —◇— 30 days, 1 min; —△— 30 days, 2 min.)

greater influence on controlling the formation of delamination.

#### 4.5.3 Effect of the BPO Catalyst on Mechanical Strength of the SMC

The BPO catalyst, the fastest catalyst in decomposition among other types of catalyst used in this research, possesses a half-life temperature in 10 hours at 73°C.

##### 4.5.3.1 Effect of the Mold Temperature on Curing Characteristic of the SMC

A convenient way to reduce the cycle time is to increase the wall temperature to match the faster curing rate at the core. Upon the investigation of the SMC processed with the BPO catalyst at the mold temperature of 150°C, the SMC part was scorched on the surface with brownish yellow color. Measurement of yellowness and whiteness indexes valued at 83.91 and -191.47, respectively, are shown in Figure 4.29. Owing to decomposition of the resin under excessive exothermic heat from the decomposition reaction of the BPO, scorched surface then occurred. The decomposition temperature of the BPO catalyst was about 110-120°C (8). Therefore, the mold temperature at 150°C was too high and unappropriated for curing the SMC using the BPO catalyst. Reducing the mold

temperature to 120°C, the SMC was then cured properly in the mold with the normal appearance; the values of the yellowness and whiteness indexes were at 20.98 and -5.44, respectively. Its mechanical properties were almost the same in comparison to those from the TBPB or DTBC catalysts. Consequently, it is appropriate to set the mold temperature at 120°C for forming the SMC with the BPO catalyst.

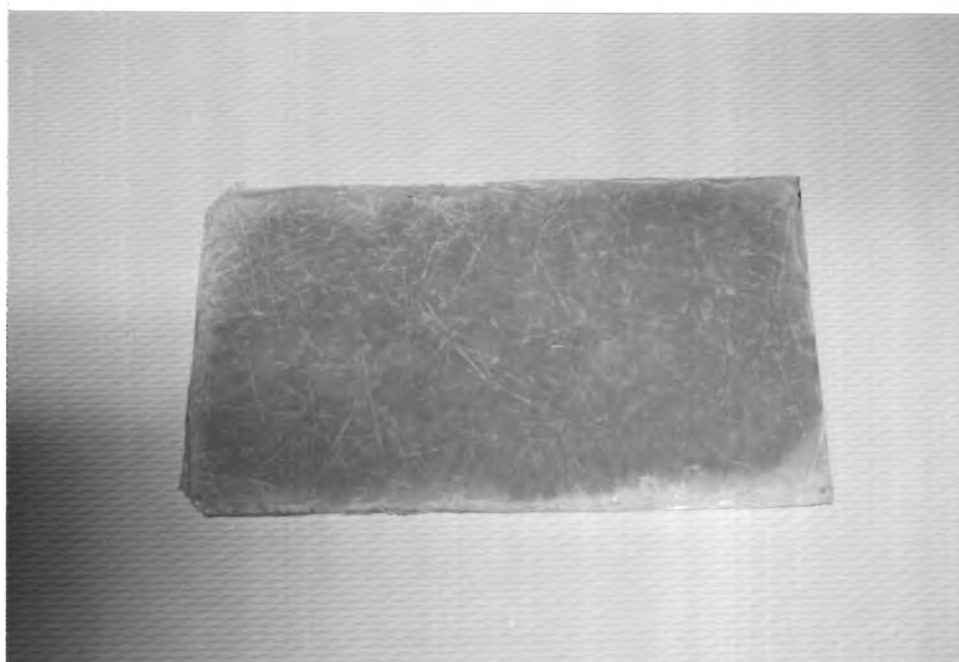


Figure 4.29 Effect of the mold temperature at 150°C on characteristic of the SMC containing the BPO catalyst (overall brownish yellow on the surface indicates the occurrence of burning).

Therefore, the selection of a suitable wall temperature must be taken into serious account for the following points: the possibility of filling the mold without premature gelling; the maximum temperature in the part must be below a level leading to degradation or undesired side reactions; and the possibility of reaching the required reaction extent at the wall (reaction not arrested by vitrification). For parts in which the core cures adiabatically, it is convenient to select a wall temperature such as that the necessary time to reach the required reaction extent will be the same at the wall and in the core. This selection may be possible when the aforementioned requirements are fulfilled. Also, when cycle time is determined by curing at the wall, it is very important not to overestimate the critical conversion needed to eject the part from the mold (28).

#### 4.5.3.2 Effect of the Concentration of BPO Catalyst on Mechanical Properties of the SMC

Regarding the concentration of BPO catalyst on the flexural strength and modulus of the SMC under the influence of the curing time of the SMC at 1 and 2 minutes, for 3 days of storage time of the SMC, the results are presented in Figures 4.30-4.31.

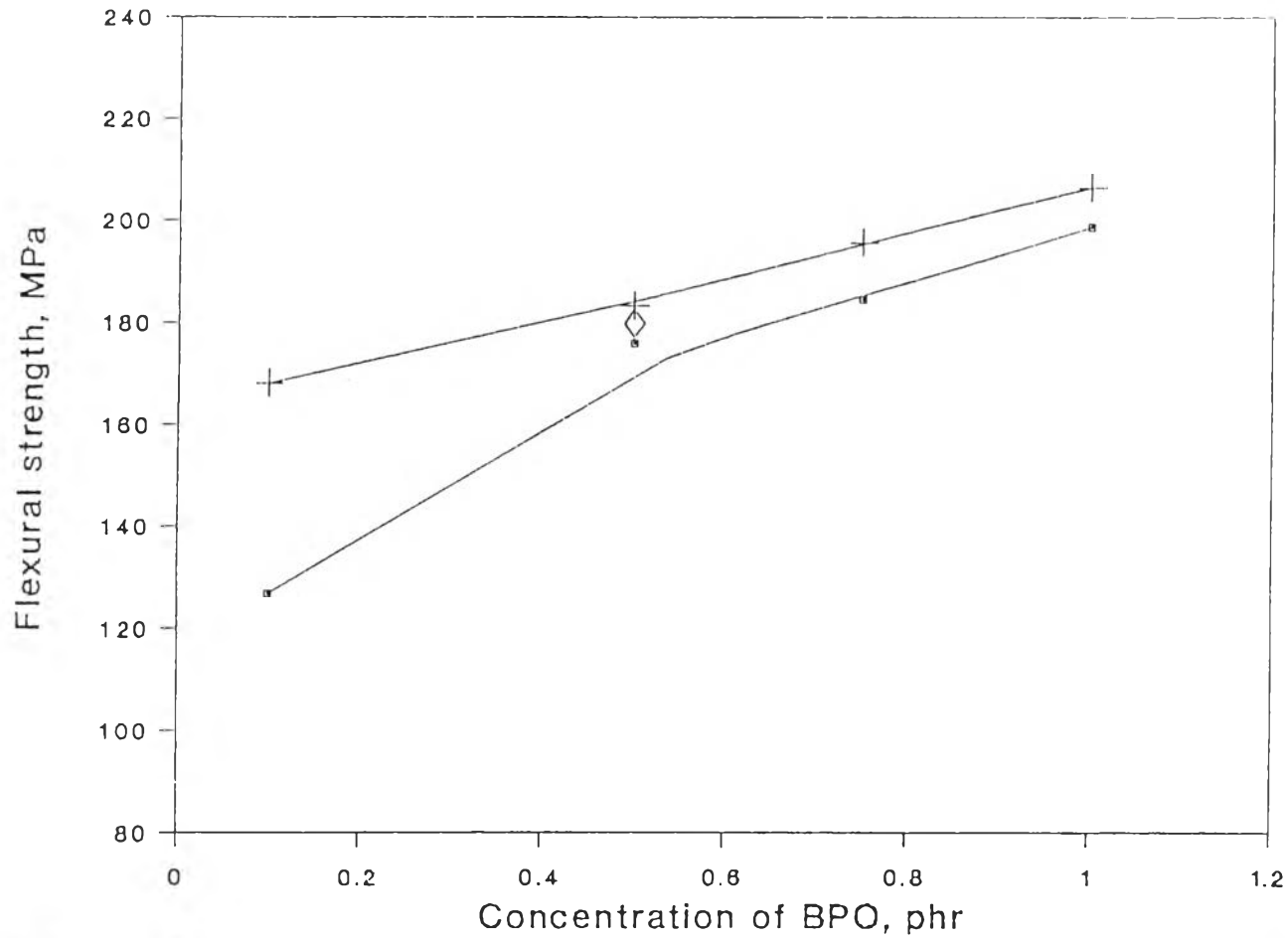


Figure 4.30 Effect of the concentrations of the BPO catalyst on the flexural strength of the SMC under the influence of the curing time for the storage time of the SMC at 3 days. ( —■— 1 min, —+— 2 min, —◇— 3 min.)



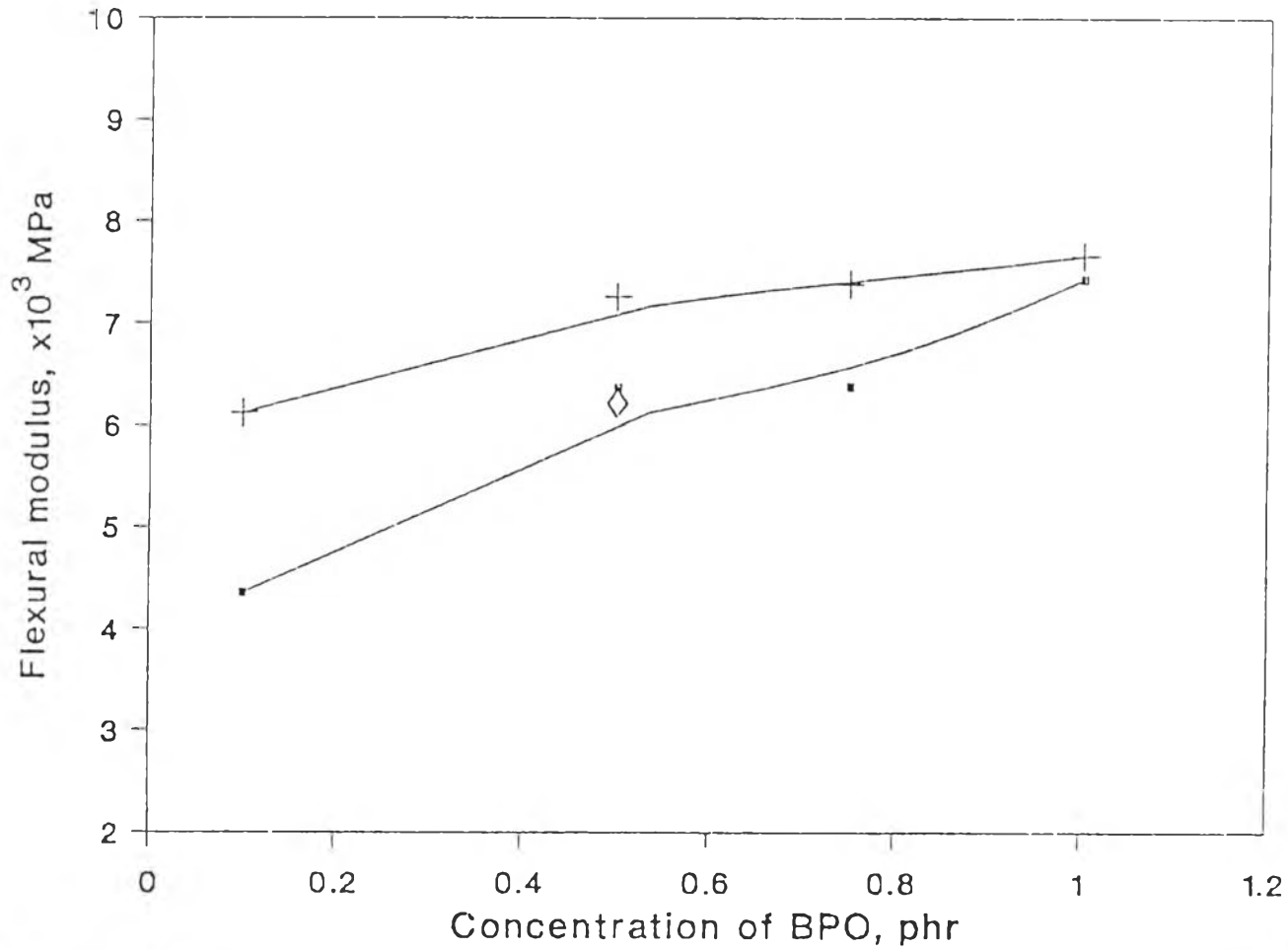


Figure 4.31 Effect of the concentrations of the BPO catalyst on the flexural modulus of the SMC under the influence of the curing time for the storage time of the SMC at 3 days. ( —●— 1 min, —+— 2 min, —◇— 3 min.)

The fundamental hypothesis was that one could use the BPO as catalyst for encouraging a faster curing time of the SMC, but from the results in Figures 4.30-4.31, the strength and modulus of the SMC were lower than those of the TBPB and DTBC catalysts. At the concentration of BPO catalyst more than 1 phr, the viscosity of paste was too high to prepare the SMC in a normal procedure. At the low concentration of 0.1 phr BPO catalyst, the viscosity of paste was decreased and the flexural strength and modulus of the SMC was consequently low as shown in Figures 4.30-4.31. The appropriate concentration of BPO was about 1.0 phr; the curing time of the SMC for 2 minutes, the flexural strength of the SMC was lower than those of the TBPB or DTBC catalyst about 20 MPa, and similarly the flexural modulus was lower than about 1,500 MPa. When considering the results of the curing time at 1 minute, the flexural strength and modulus of the SMC obtained was also lower than the 2 minutes of curing time. However, the flexural strength and modulus were in the range of acceptable value when compared with the mechanical properties of the SMC in the literature elsewhere (1).

#### 4.5.4 Effect of the Added Parabenzquinone (PBQ) on Mechanical Properties of the SMC

The PBQ was a kind of inhibitor which could be filled in the polyester resin to decrease an excessive polymerization reaction and to extend the storage time of

the SMC (6).

In this study, the PBQ was added in the component of the SMC with the concentrations of 0.025 and 0.05 phr. Then the composite was kept for 17 days at room temperature. The results of flexural strength and modulus of the SMC at the curing time in the mold of 1 and 2 minutes were shown in Table 4.2.

From the results in Table 4.2, the added PBQ in the component of the SMC decreased the hardness of the SMC sheet. It could simultaneously extend the storage time of the SMC and yet it did not decrease the mechanical properties of the SMC. These results might come from the inhibition reaction of the PBQ in which the inhibitor stopped the polymerization reaction of chain propagation of the radicals produced by the catalyst during storage. The stability of the catalyst was increased. Moreover, it normally decreased the effect of exothermic heat imposing during the curing reaction of the resin by decreasing cracking or crazing in the cured SMC (11). The flexural strength and modulus of the SMC with only 1 minute curing time was almost equal to that of the 2 minutes curing time.

Table 4.2

Effect of the added PBQ in the component of the SMC on  
flexural strength and modulus of the SMC.

Type of catalyst	Concentrations		Hardness (Shore A)	1 min Cure time		2 min Cure time		1 min Cure time		2 min Cure time	
	Catalyst (phr)	PBQ (phr)		Flexural strength		Flexural strength		Flexural modulus		Flexural modulus	
				$\bar{X}_{FS}$ (MPa)	Std.dev.	$\bar{X}_{FS}$ (Mpa)	Std.dev.	$\bar{X}_{FM}$ (MPa)	Std.dev.	$\bar{X}_{FM}$ (Mpa)	Std.dev.
TBPB	2	-	60-65	202.16	19.60	233.05	5.73	8927.23	5.73	9416.91	748.50
TBPB	2	0.025	55-60	199.27	5.06	243.12	10.31	8296.77	198.32	9853.58	622.29
TBPB	2	0.050	55-60	237.82	14.18	247.16	19.98	11822.82	1068.50	9627.16	308.30
DTBC	2	-	65-70	181.27	7.34	204.23	16.43	7404.39	410.36	8137.66	733.19
DTBC	2	0.025	60-65	206.13	10.80	206.37	27.39	8112.49	554.54	8211.76	441.29

Note :  $\bar{X}_{FS}$  and  $\bar{X}_{FM}$  stand for an average value of flexural strength and modulus, respectively for 4 measurements.

Due to that the inhibitors are capable of preventing the cure reaction by reacting with free radicals generated in the system, they provide an induction time (or inhibition period) for the compound to fill the mold without any scorch problem. At high temperatures, the catalysts are more active and can generate more free radicals rapidly, therefore, the induction time will be shorter accordingly. At lower temperatures, an opposite result may occur. For an ideal SMC compound, the induction time should be long enough to ensure complete mold filling, yet short enough to achieve a short cure time (12). The other result of adding PBQ in the component of SMC was in that the original yellow color became very strong. The yellowness index was increased from 15.55 to 39.88 and whiteness index was decreased from -1.31 to -51.21. The change of color does affect the product's appearance in terms of hue, saturation and lightness/brightness.

#### 4.5.5 Effect of the Dual Catalysts on Mechanical Properties of the SMC

To reduce the cure time of the SMC obtained with a single catalyst, dual catalyst systems are often used. One of the more common SMC catalyst combinations today is t-butyl peroctoate (TBPO) with a half life temperature of 74°C, used in conjunction with t-butyl perbenzoate (TBPB) (1).

In this study, the dual catalyst systems consisting of the 1,1-di-(t-butyl peroxy) cyclohexane (DTBC) in conjunction with the TBPB catalyst were used in the composition of SMC. Various combinations of these two catalysts on the effect of mechanical properties of the SMC were investigated. Results are shown in Table 4.3. The flexural strength averages ranging from 170 to 210 MPa for 1 minute of curing time and from 210 to 230 MPa for 2 minutes of curing time were obtained. The flexural moduli are ranging from 7000 to 8500 MPa for 1 minute of curing time and from 8000 to 9000 MPa for 2 minutes of curing time. The only significantly increased mechanical properties appeared to be the formulation containing the highest level (1.5 phr) of the DTBC catalyst. However, the result of the 1 minute of curing was remained lower than that of the 2 minutes of curing time. In conclusion, the dual catalyst system indeed cures the SMC much faster than does the TBPB alone.

Table 4.3

Effect of dual catalysts of TBPB and DTBC on the mechanical properties of the SMC.

Concentrations of		Storage time (days)	1 min Cure time		2 min Cure time		1 min Cure time		2 min Cure time	
TBPB	DTBC		Flexural strength		Flexural strength		Flexural modulus		Flexural modulus	
(phr)	(phr)		$\bar{X}_{FS}$ (MPa)	Std.dev.	$\bar{X}_{FS}$ (Mpa)	Std.dev.	$\bar{X}_{FM}$ (MPa)	Std.dev.	$\bar{X}_{FM}$ (Mpa)	Std.dev.
1.0	-	3	193.87	13.52	222.30	20.69	7947.07	541.53	8585.53	967.71
-	1.0	3	206.91	24.79	212.78	12.12	7922.13	1002.73	7456.57	300.81
0.5	0.5	3	189.23	10.26	209.48	12.95	8009.48	479.15	8273.00	884.05
1.5	0.5	3	175.15	7.47	213.03	14.48	6424.96	482.35	7571.33	1160.92
1.0	1.0	3	171.59	4.28	208.81	7.72	6805.75	1099.44	8055.58	993.80
0.5	1.5	3	172.20	15.37	218.78	13.42	7008.14	654.50	8076.28	880.54
2.0	-	3	186.34	8.41	208.79	11.78	7107.24	464.97	7774.46	472.85
-	2.0	3	183.07	13.59	205.33	9.36	6614.72	1880.51	7002.47	879.91

Note :  $\bar{X}_{FS}$  and  $\bar{X}_{FM}$  stand for an average value of flexural strength and modulus, respectively for 4 measurements.

(P.T.O.)

Table 4.3 (Continued).

Concentrations of		Storage time (days)	1 min Cure time		2 min Cure time		1 min Cure time		2 min Cure time	
TBPB	DTBC		Flexural strength		Flexural strength		Flexural modulus		Flexural modulus	
(phr)	(phr)		$\bar{X}_{FS}$ (MPa)	Std.dev.	$\bar{X}_{FS}$ (Mpa)	Std.dev.	$\bar{X}_{FM}$ (MPa)	Std.dev.	$\bar{X}_{FM}$ (Mpa)	Std.dev.
1.0	-	17	208.17	20.27	224.14	3.25	7515.51	569.23	8774.51	385.77
-	1.0	17	189.03	20.12	214.78	12.12	7404.39	410.36	8137.66	733.19
0.5	0.5	17	185.92	15.68	222.46	16.06	7036.46	850.76	8662.36	1268.98
1.5	0.5	17	199.57	16.89	238.62	13.52	7167.32	899.22	8480.30	902.23
1.0	1.0	17	218.76	6.98	223.07	12.09	8506.31	1094.48	8753.30	965.46
0.5	1.5	17	197.46	22.56	220.34	11.90	8188.16	862.33	8669.23	579.68
2.0	-	17	202.16	19.60	233.05	5.73	8927.23	573.78	9416.91	748.50
-	2.0	17	181.27	7.34	204.23	16.43	7404.39	410.36	8137.66	733.19

Note :  $\bar{X}_{FS}$  and  $\bar{X}_{FM}$  stand for an average value of flexural strength and modulus, respectively for 4 measurements.

(P.T.O.)



Table 4.3 (Continued).

Concentrations of		Storage time (days)	1 min Cure time		2 min Cure time		1 min Cure time		2 min Cure time	
TBPB	DTBC		Flexural strength		Flexural strength		Flexural modulus		Flexural modulus	
(phr)	(phr)		$\bar{X}_{FS}$ (MPa)	Std.dev.	$\bar{X}_{FS}$ (Mpa)	Std.dev.	$\bar{X}_{FM}$ (MPa)	Std.dev.	$\bar{X}_{FM}$ (Mpa)	Std.dev.
1.0	-	30	168.71	17.50	202.14	7.41	7036.20	386.20	7693.14	1226.57
-	1.0	30	178.24	14.97	192.04	3.80	7097.19	451.47	7443.79	80.03
0.5	0.5	30	190.06	17.16	239.09	13.58	7144.48	1513.81	9063.69	994.74
1.5	0.5	30	205.17	14.17	242.96	9.64	7568.13	568.00	8806.11	254.51
1.0	1.0	30	207.07	19.04	223.35	9.62	7389.57	1022.00	8279.67	206.84
0.5	1.5	30	207.94	17.63	229.33	16.27	7829.12	944.79	8312.45	581.53
2.0	-	30	215.32	10.00	250.47	3.23	8956.74	499.21	9819.91	52.74
-	2.0	30	179.47	4.89	200.53	22.29	7316.42	442.20	7799.64	238.17

Note :  $\bar{X}_{FS}$  and  $\bar{X}_{FM}$  stand for an average value of flexural strength and modulus, respectively for 4 measurements.

#### 4.6 Effect of Catalyst on Adhesion Properties between Matrix and Fiber

The mechanical properties of composites are dependent upon the adhesion of the matrix resin to the fibers. Bond formation can only take place while the liquid resin and reinforcement are in contact. The reduction in cycle times needed to make the SMC process viable for volume manufacturing means that the liquid resin may only in contact with the fibers for a few seconds. During this time the resin must wet the fibers and form the interfacial bonds. The mechanical properties of the material depend upon the efficient transfer of stress across such an interface (29).

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 contributing 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 (30). 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 underload and utilized as structural SMC application (31).

In addition, the cracking surface of the specimen which was passed the mechanical strength tests as photographed by Scanning Electron Microscopy (SEM) for studying the microstructure characteristics of adhesion between the matrix and glass fiber. The aim of this investigation was to discover what effect the reduction in cycle time had on the adhesion of the matrix resin to the glass fiber. For the purpose of the investigation, wet-through and wet-out have the following definitions. Wet-through (29) has occurred when the resin has displaced all of the air from, within a reinforcement mat, glass fiber, and is able to surround the fibers. Wet-out has occurred when the resin has wetted and bonded to the individual fibers. Complete wet-out is often considered to be shown by translucence of the matrix and fibers (fiber disappearance). The end of wet-through and the start of wet-out are indistinct since the two processes usually occur concurrently.

The studies were made by the 500-1,000 magnification ratio of the sample photomicrographs which has high mechanical strength comparing with low mechanical strength because of the effect of various variables as shown in Figures 4.32 to 4.35.

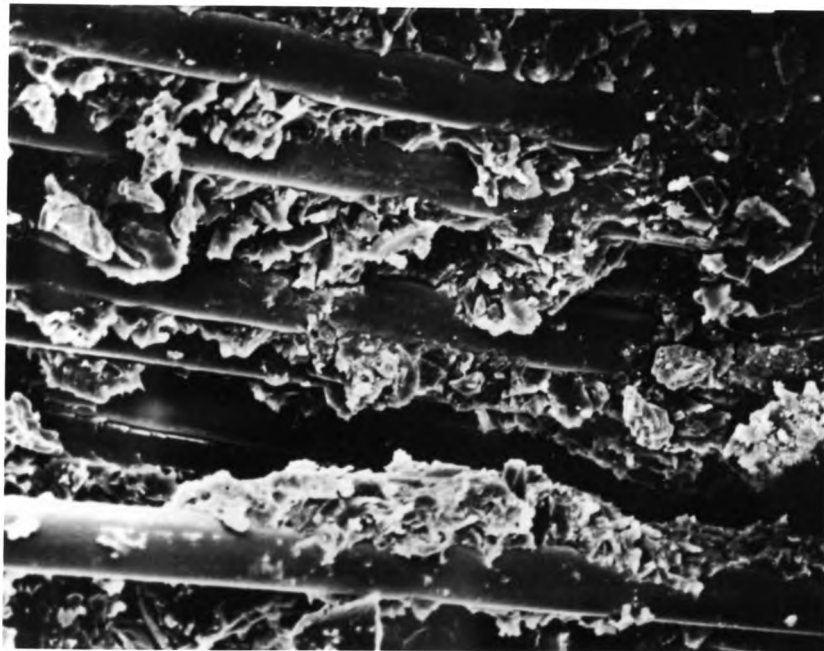


Figure 4.32 Scanning electron micrograph (at 500 x) of the fracture surface of the high mechanical property SMC was produced by 1 minute of curing time; containing 2 phr of the TBPB catalyst added with 0.05 phr PBQ, having the flexural strength of 237.8 MPa. The SEM micrograph shows a little wet-out, but a full wet-through.



Figure 4.33 Scanning electron micrograph (at 1000 x) of the fracture surface of the high mechanical property SMC was produced by 2 minutes of curing time; containing 2 phr of the TBPB catalyst added with 0.05 phr PBQ, having the flexural strength of 247.2 MPa. The SEM micrograph shows a little wet-out, but a full wet-through.

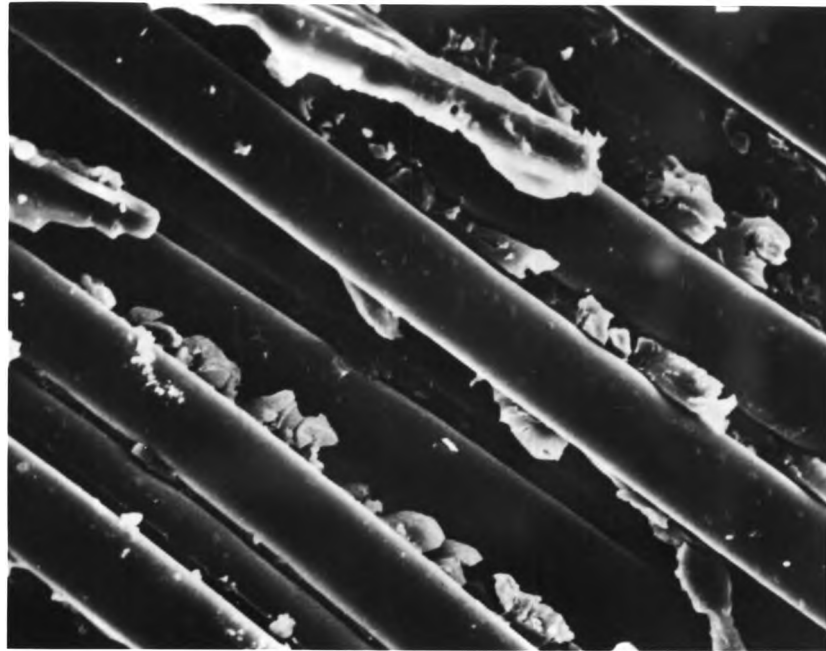


Figure 4.34 Scanning electron micrograph (at 1000 x) of the fracture surface of the low mechanical property SMC was produced by 1 minute of curing time; containing 0.5 phr of the TBPB catalyst, having the flexural strength of 152.5 MPa. The SEM micrograph shows both a poor wet-out and wet-through.

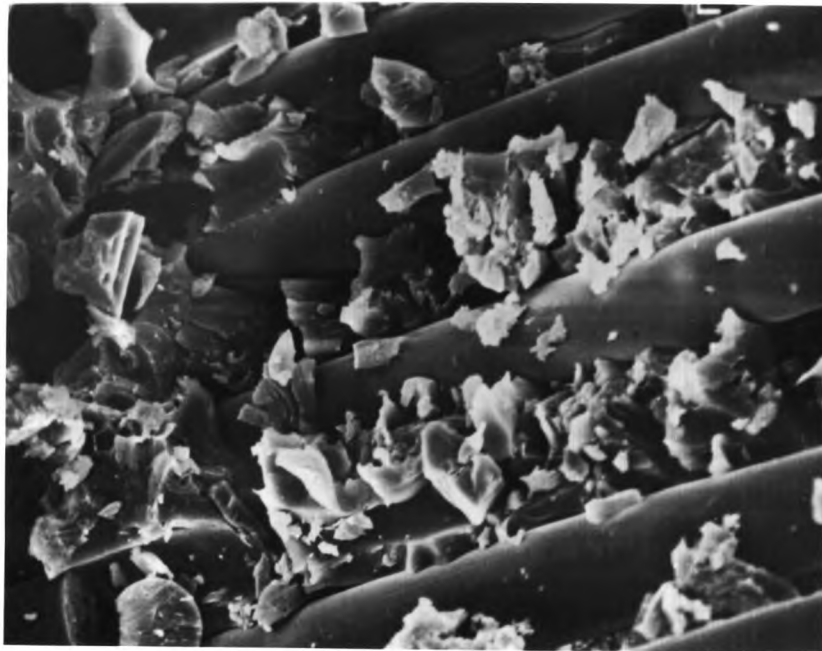


Figure 4.35 Scanning electron micrograph (at 1000 x) of the fracture surface of the SMC was produced by 2 minutes of curing time; containing 1 phr of the TBPB catalyst, having the flexural strength of 222.3 MPa. The SEM micrograph shows a little wet-out, but a full wet-through.

It has been demonstrated that the cure times of 1 and 2 minutes are feasible using hot setting resins. During a 1 minute, cure contract times are significantly reduced when compared to cure time of 2 minutes. The SEM pictures at a magnification of 1000 times show similar clean fibers for both conditions of curing time, regardless of the wet-out time. The fracture surface of the high flexural loading of the SMC sample, containing 2 phr of the TBPB catalyst, together with the addition of 0.05 phr PBQ inhibitor at the curing times of 1 and 2 minutes were shown in Figures 4.32-4.33, respectively. This suggests a low interfacial strength for the 1 minute of curing time specimen; in contrast, the 2 minutes of curing time specimen demonstrates a successful wet-through by the deposition of the resin on the fiber surfaces. The fracture surface of the low mechanical properties SMC, containing 0.5 phr of the TBPB catalyst under the curing time of 1 minute and 2 minutes were shown in Figures 4.34-4.35. All of the moldings produced had visible fibers when viewed with transmitted light, this may be due to the lack of fiber wet-out, or it may be due to de-bonding as a result of differential thermal shrinkage (29).

According to the results in Figures 4.32-4.35, it is inevitable that the mechanical strength of the SMC relate to the adhesion properties between the matrix and glass fiber. The material with the high mechanical strength would normally have better adhesion between resin



and fiber than that with low mechanical strength. The cause might come from various variables such as type and concentration of catalysts, storage time, and curing time in the mold of the SMC. Since the curing is still the phenomenon of the polymerization reaction, it is also dependent on cure time, temperature, and concentration of reactants. Alteration of the first two variables provides the basic mechanism for controlling the processing of curable resin (29). The use of 1 minute curing time, the adhesion or wet-through and wet-out between the resin and fiber were not complete and good. The wet-out can take place and bonds may form, but only if sufficient time is available. It is also possible that incomplete wet-through may prevent full wet-out from occurring (29).