# CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Synthesis of 2,2-Bis[4-(2-hydroxypropoxy)phenyl]propane

2,2-Bis[4-(2-hydroxypropoxy)phenyl]propane was prepared by the reaction of a mixture of 1 mole of bisphenol A and 2 mole of propylene oxide in the presence of alkaline catalyst, sodium hydroxide solution, in water media.

bisphenol A   propylene oxide

NaOH/H$_2$O

2,2-bis[4-(2-hydroxypropoxy)phenyl]propane
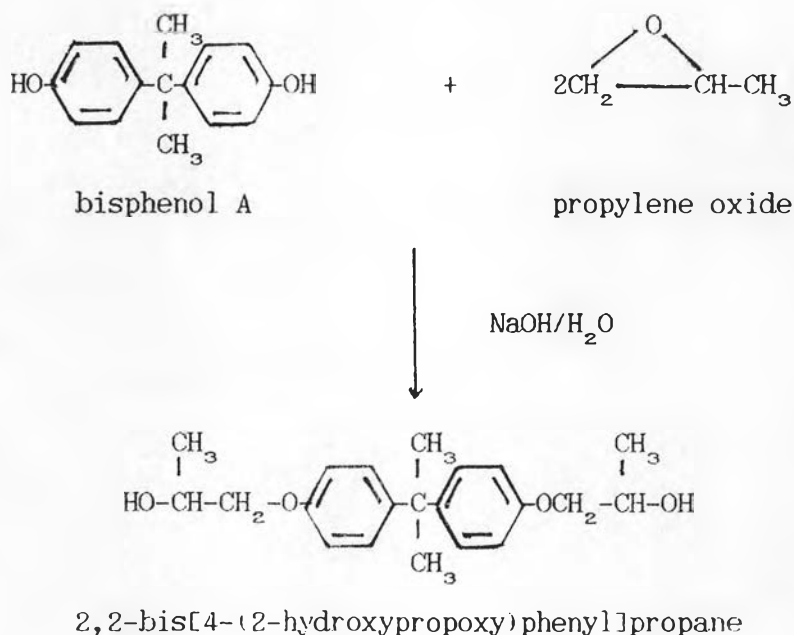
Thin-layer chromatographic technique was used to monitor the reaction. By using chloroform : methanol (6:1) as the developing solvent, it appearred 2 spots at R$_F$ value 0.33 and 0.45 which corresponded to bisphenol A and 2,2-bis[4-(2-hydroxypropoxy)phenyl]propane, respectively. Thin layer chromatography thus confirmed that the product had been formed.

This product was viscous liquid with light yellow color or clear color as crystal. After prolong storage, it was changed to wax-liked. It had a melting temperature at about 57-58°C. Its solubility was tested as shown in Table 4.1. The results were agree with the reported data in reference 39 as the product had excellent solubility in aromatic hydrocarbon in aromatic hydrocarbon, alcohol, acetone, ether, tetrahydrofuran but non-soluble in hexane, and water.

Table 4.1 Solubility of reactant (bisphenol A and propylene oxide) and 2,2-bis[4-(2-hydroxypropoxy)phenyl]propane

Solvents	Bisphenol A	Propylene Oxide	Products
acetone	very good	very good	very good
benzene	bad	bad	very good
carbon tetrachloride	bad	bad	good
chloroform	good	very good	very good
cyclohexane	bad	bad	bad
N,N-dimethylformamide	very good	very good	very good
ethanol	very good	very good	very good
diethylether	very good	very good	very good
hexane	bad	bad	bad
methanol	very good	very good	very good
methylene chloride	good	very good	very good
petroleum ether	bad	bad	bad
toluene	bad	bad	very good
water	bad	good	bad

Identification of this product was compared with bisphenol A by using IR, NMR, GC and DTA analysis. IR (KBr) spectrum of bisphenol A and IR (NaCl) spectrum of 2,2-bis[4-(2-hydroxypropoxy)phenyl]propane were exhibited in Figure 4.1-4.2, respectively. The absorption band of these substances were similar, thus this technique cannot identify the difference of structure of bisphenol A and 2,2-bis[4-(2-hydroxypropoxy)phenyl]propane. The absorption bands of these substances were interpreted in Table 4.2.

Table 4.2 The assignment for the IR spectrum of bisphenol A
and 2,2-bis[4-(2-hydroxypropoxy)phenyl]propane

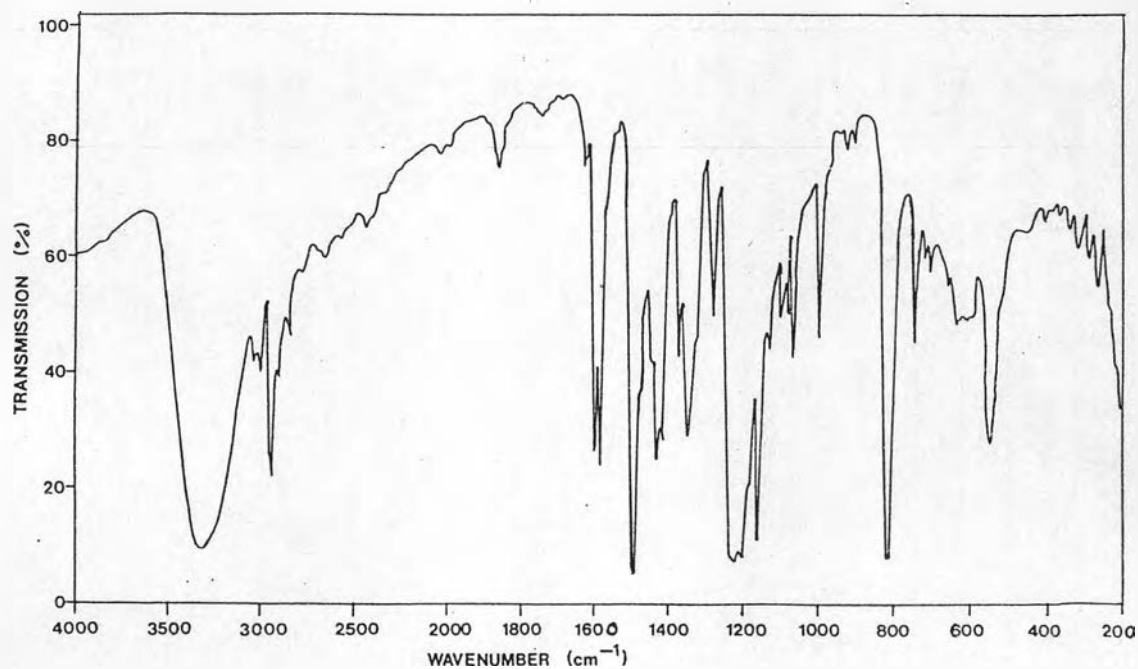| Absorption frequency $\mathcal{V}$ (cm^{-1})	Assignment
3600 - 3200	H - bonded -OH group
3050	C - H stretching in aromatic
2900	C - H stretching in aliphatic
2000 - 1667	para - disubstituted overtone in benzene ring
1600 , 1400	C = C stretching in aromatic
1500	C - H bending ($>CH_2$, $-CH_3$)
1230	C - O stretching

Figure 4.1 IR (KBr) spectrum of bisphenol A

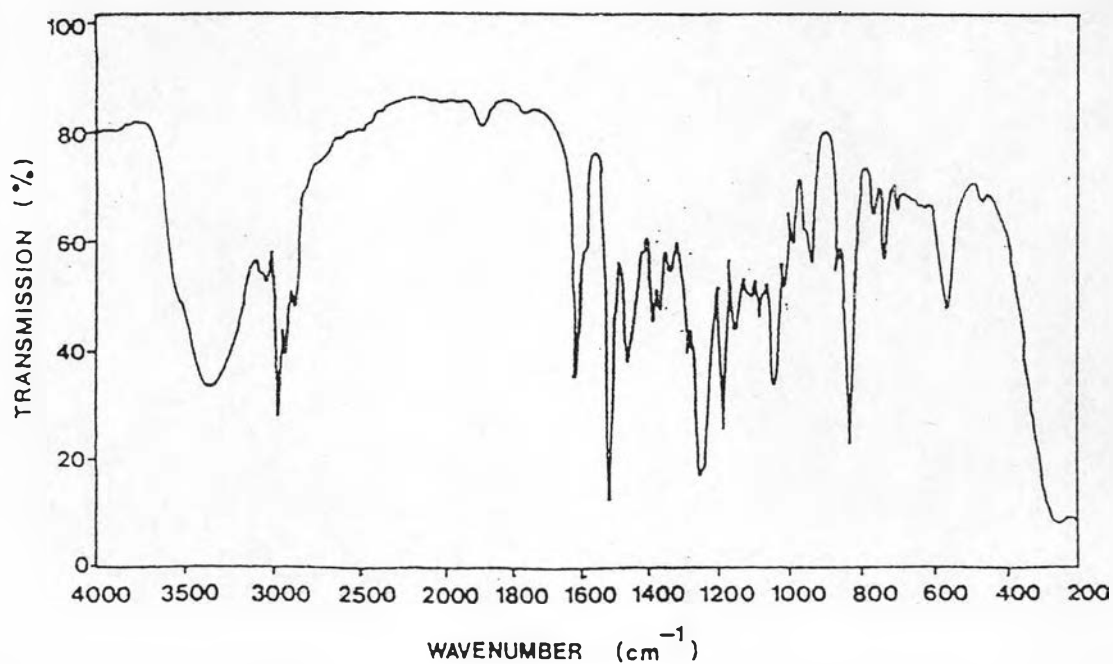Figure 4.2 IR (NaCl) spectrum of

2,2-bis[4-(2-hydroxypropoxy)phenyl]propane

The ^{1}H-NMR spectrum for bisphenol A and 2,2-bis-[4-(2-hydroxypropoxy)phenyl]propane were exhibited in Figure 4.3-4.4, respectively. The difference between these substances can seen clearly by NMR spectrum. The signals of the similar protons of these substances were slightly changed the chemical shifts as shown in Table 4.3-4.4, respectively. The ^{1}H-NMR spectrum of 2,2-bis[4-(2-hydroxypropoxy)phenyl]propane showed the signals at δ 4.13, 3.90, 3.75, and 1.18 ppm which corresponded to protons of the propoxy groups and the signals of hydroxyl group was shift to high field at δ 2.49 ppm. Consequently, the ^{1}H-NMR spectrum in Figure 4.4 was confirmed that it was a structure of 2,2-bis[4-(2-hydroxypropoxy)phenyl]propane.
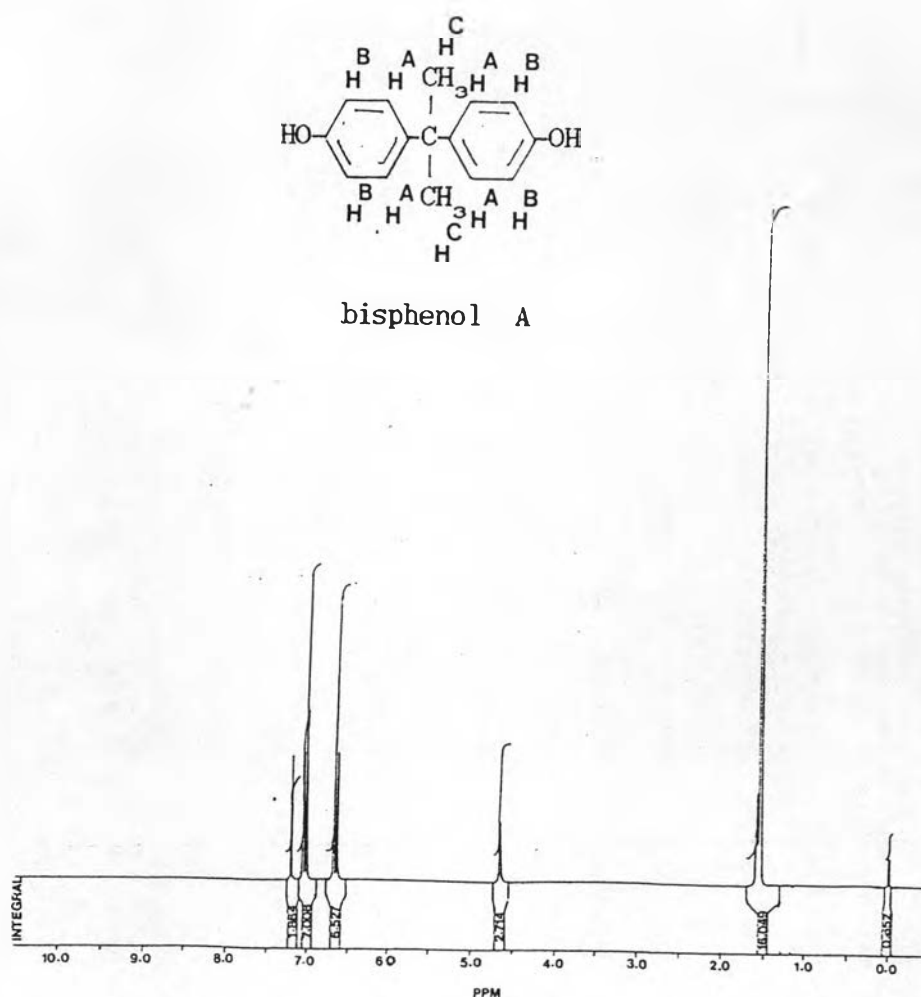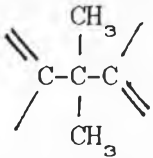

bisphenol A

Figure 4.3 ^{1}H-NMR (CDCl$_3$) spectrum of bisphenol A

Table 4.3 The assignment for the ^{1}H-NMR spectrum of bisphenol A

Chemical shift δ (ppm)	Assignment
7.05	meta proton [H^B]
6.70	ortho proton [H^A]
4.65	-OH
1.55	[structure] [H^C]

2,2-bis[4-(2-hydroxypropoxy)phenyl]propane
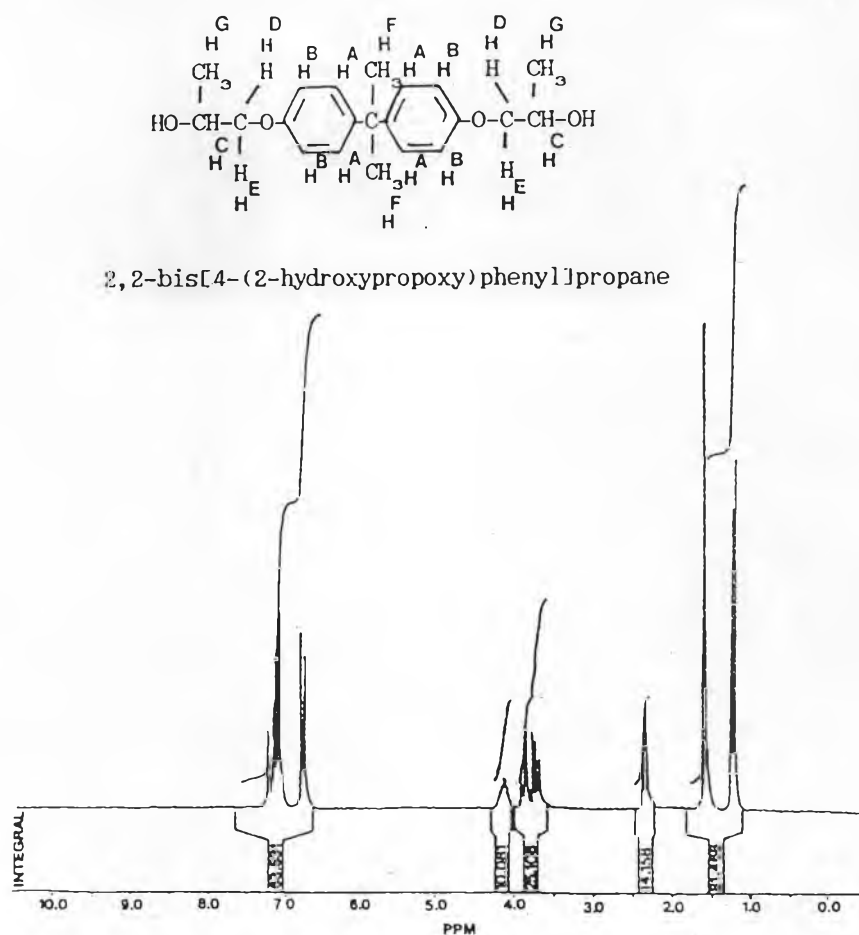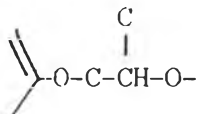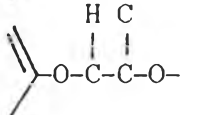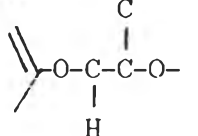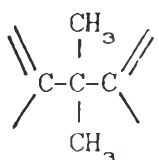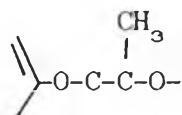

Figure 4.4 ^{1}H-NMR (CDCl$_3$) spectrum of

2,2-bis[4-(2-hydroxypropoxy)phenyl]propane

Table 4.4 The assignment for the ^{1}H-NMR spectrum of

2,2-bis[4-(2-hydroxypropoxy)phenyl]propane

Chemical shift δ(ppm)	Assignment
7.16	meta proton [H^B]
6.75	ortho proton [H^A]
4.13	C | 〉-O-C-CH-O- [H^C]
3.90	H C | | 〉-O-C-C-O- [H^D]
3.75	C | 〉-O-C-C-O- [H^E] | H
2.49	-OH
1.55	CH$_3$ | 〉C-C-C〈 [H^F] | CH$_3$
1.25	CH$_3$ | 〉-O-C-C-O- [H^G]

The GC chromatogram for 2,2-bis[4-(2-hydroxypropoxy)-phenyl]propane was shown (Figure 4.5) the retention time at 27.45 minute and the solvent retention time of ethanol was appeared at 0.46 minute but bisphenol A has the retention time at 16.95 minute. From this chromatogram is shown that the synthetic monomer has high purity.
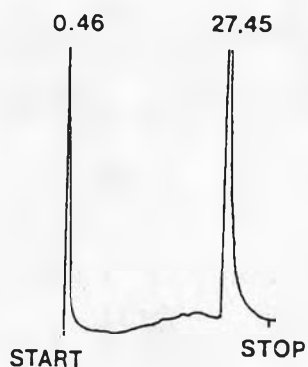
0.46   27.45

START   STOP

Figure 4.5 GC chromatogram of
            2,2-bis[4-(2-hydroxypropoxy)phenyl]propane

When   2,2-bis[4-(2-hydroxypropoxy)phenyl]propane   was
heated   under atmosperic pressure   and temperature   100-250°C, it
does not change characteristic   and properties. Figure 4.6 showed
that   this   monomer   had   melting   temperature   about   57-58°C
and decomposed at 300°C, but bisphenol A had   decomposition
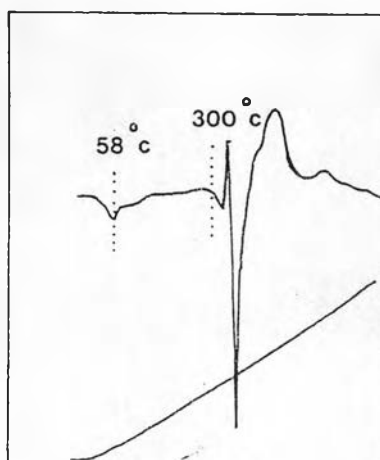temperature at 250°C. Thus the advantage of this monomer was
high heat resistance.

58°c   300°c

Figure 4.6 Differential thermal analysis thermogram of
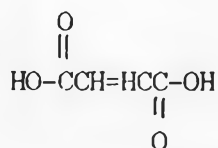   2,2-bis[4-(2-hydroxypropoxy)phenyl]propane

4.2 Synthesis of Self-emulsifiable Unsaturated Polyester Resin

The unsaturated polyesters are derived from a production process which involves the condensation esterification of dihydric alcohols and dicarboxylic acids. Alteration of the chemical structure by processing techniques and raw material selection is a method of achieving the desired properties in the formulated resins.

The most commonly used unsaturated acids are fumaric acid and maleic anhydride. Maleic anhydride is the most economic derivative but fumaric acid can be substituted maleic anhydride because it tends to give lighter coloured products (24). They confer the fundamental unsaturation to the polyester, which provides the reactivity with coreactant monomers such as styrene.
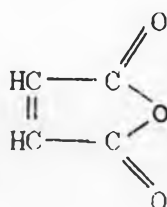
Self-emulsifiable unsaturated polyester resin was prepared by the reaction of a mixture of 1 mole of fumaric acid or 1 mole of maleic anhydride and 1.05 mole of 2,2-bis[4-(2-hydroxypropoxy)phenyl]propane in the presence of polyethylene glycol number 1500 that acted as emulsifier which allowed to participate in the reaction, whereby a self-emulsifiable polyester is obtained because polyethylene glycol will increase the sensitivity of polyester to water. The hydrophilic groups, polyethylene glycol, was introduced into the polymer chain or in side chain to prepared water-soluble polyesters (42). However, the emulsifier was utilized in small quantity because of it does not substantially increase the water sensitivity of the cured films which are ultimately obtained when these polyesters were used as film-forming agent on glass fiber surface. Hydroquinone was added to the reaction to prevent

gelation at high process temperature. The structure of both unsaturated polyester resins have similar model shown as follows :
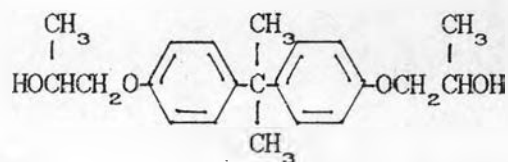
$$
\begin{array}{c}
O \\
\parallel \\
HO-CCH=HCC-OH \\
\parallel \\
O
\end{array}
$$

fumaric acid

or   +

$$
\begin{array}{c}
O \\
\nearrow \\
HC \longrightarrow C \\
\parallel \quad \diagdown O \\
HC \longrightarrow C \\
\diagdown \\
O
\end{array}
$$

2,2-bis[4-(2-hydroxypropoxy)phenyl]propane
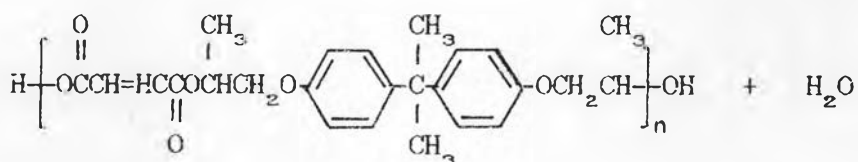
maleic anhydride

unsaturated polyester resins

Maleic anhydride exists in a planar configuration of low conformational energy, and the conversion into maleate diesters and oligomers during the initial esterification reaction increases the strain energy across the double bond because of steric hindrance. At lower reaction temperature, i.e. $160^\circ C$, the maleate esters remain in this condition,, but as the reaction temperature exceeds $180^\circ C$, they effectively relieve the strain by transforming to the more planar trans-fumarate isomer, which reduces the steric congestion (26).

maleic anhydride   cis-maleate ester   trans-fumarate
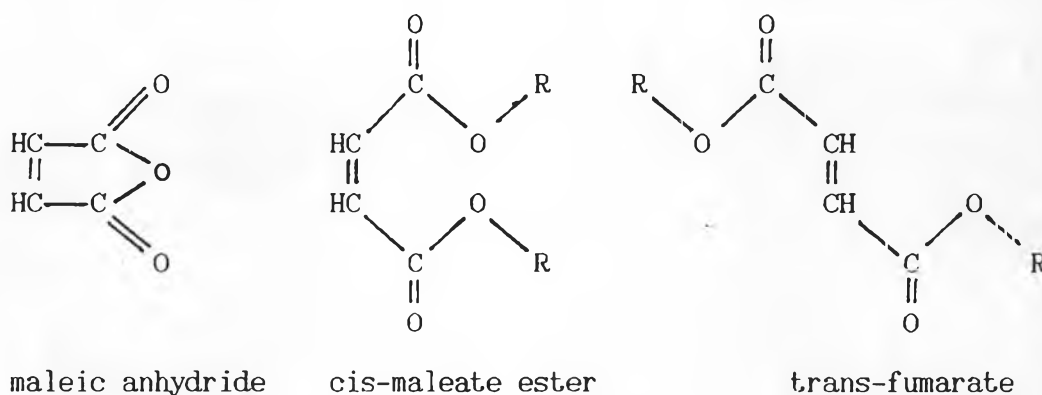
In conventional fusion melt, the long reaction time, usually at temperature above $180^{\circ}C$, causes the maleate ester to isomerize to the corresponding fumarate. This isomerization during the polyesterification process is of fundamental importance in the development of optimum physical characteristics. The isomerization of maleate to fumarate may only be partially completed, which is reflected in the product. Maleate esters, because of the increased strain across the double bond, are distorted slightly from a planar configuration, which suppresses their ability to copolymerize with styrene. The corresponding fumarate polymers are subject to less steric interference in the trans form and are able to assume a planar configuration, displaying reactivities almost 20 times those of the maleate reaction products in subsequent copolymerization reactions with styrene (25).

The extra advantage of this formula is the increment of an alkali resistance which is the principal deficiency of polyester resins. The ester linkages are subject to hydrolysis in the presence of the alkali. Increasing the size of the glycol has the effect of reducing the concentration of ester linkages. Thus, 2,2-bis[4-(2-hydroxypropoxy)phenyl]propane is able to separate ester linkages to increase an alkali resistance of

polyester resins (27,43). It is a good adhesive compound by bisphenol A imparts the ability for better bonding to metal, glass, and other substances (44). Furthermore, the incorporation of this monomer into the resin system is claimed to impart to enhancements in flexibility, shelf-life, and processability of the resin systems (45,46)

During the reaction, acid number of polyester was determined every hour (Figure 4.7). When the acid number of the reaction mixture becomes lower than 25, the reaction was stopped. These products appeared to be highly viscous liquids, light yellow color for polyester from fumaric acid and intense yellow color for polyester from maleic anhydride. Both of them also have a softening point at 95°C.
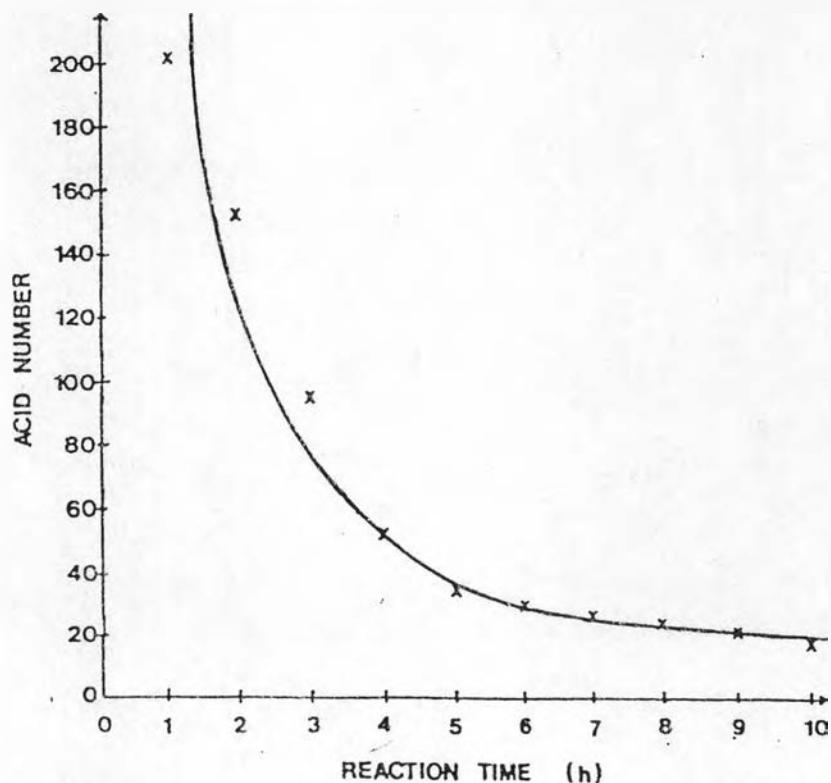

Figure 4.7 Determination of acid number during preparation of both unsaturated polyester resins

IR (NaCl) spectrum of both the unsaturated polyester resin has similar characteristic (Figure 4.8-4.9), thus this technique cannot identify the difference structure of both polyester resins. The absorption bands in these spectrum were interpreted in Table 4.5. The absorption band at $J = 2000\text{-}1667$ cm^{-1} which indicated the appearance of the para-disubstituted overtone in benzene ring couldnot be observed from the IR spectrum because it was shielded by the absorption band of carbonyl group. The absorption bands at $J = 1600$, 1450, and 830 cm^{-1} which indicated the appearance of double bond and the absorption band at $J = 1725$ cm^{-1} which indicated the appearance of carbonyl group confirmed that there were unsaturated polyester resins.

Table 4.5 The assignment for the IR spectrum of both unsaturated polyester resins

Absorption frequency J (cm^{-1})	Assignment
3600 - 3200	H - bonded - OH group
3050	C - H stretching in aromatic
2900	C - H stretching in aliphatic
1725	C = O stretching in aliphatic
1600 , 1450	C = C stretching in aromatic
1500	C - H bending ($\diagdown$CH$_2$, -CH$_3$)
1300 - 1210	C-O-C asymmetric stretching
1190 - 1090	C-O-C symmetric stretching
830	C = C stretching in aliphatic

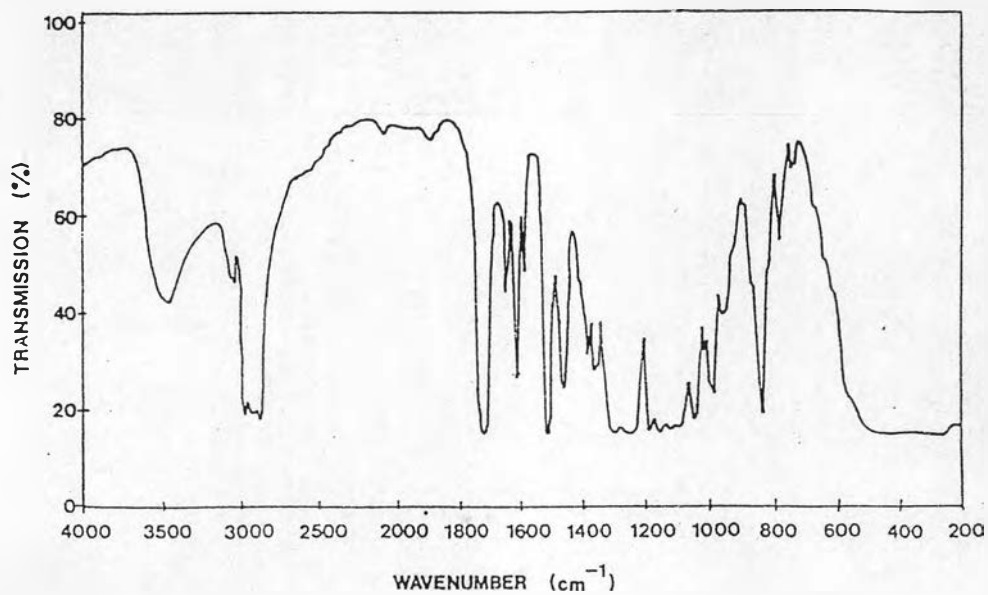Figure 4.8 IR (NaCl) spectrum of polyester from fumaric acid
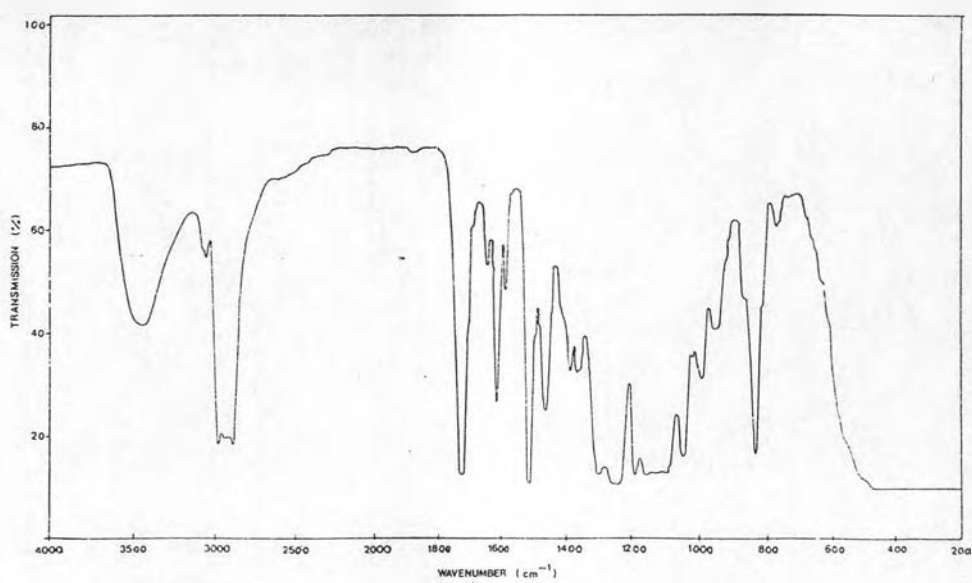
Figure 4.9 IR (NaCl) spectrum of polyester from maleic anhydride

The ^{1}H-NMR spectrum of polyester from fumaric acid and maleic anhydride were exhibited in Figure 4.10-4.11, respectively. The difference between both polyesters can be seen clearly by NMR spectrum. The signals of the similar protons of both polyesters were slightly changed the chemicals shifts as shown in Table 4.6-4.7, respectively. The ^{1}H-NMR spectrum of polyester from fumaric acid (Figure 4.10) was shown the signal at δ 1.30 ppm which corresponded to proton of methyl group and was overlapped with the signal of olefinic proton (trans-isomer carbonyl group), thus this signal was induced to high intensity.

polyester from fumaric acid
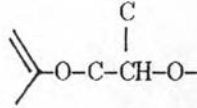
Figure 4.10 ^{1}H-NMR (CDCl$_3$) spectrum of polyester from fumaric acid

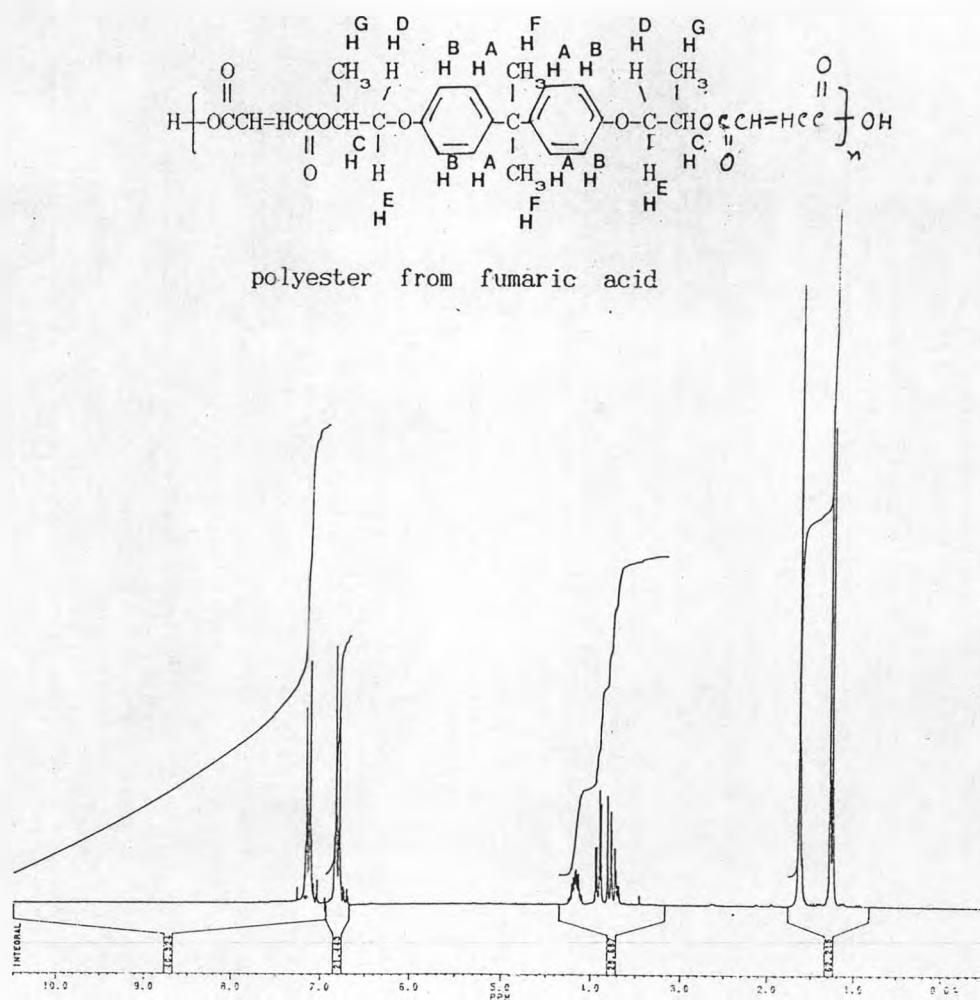Table 4.6 The assignment for the ^{1}H-NMR spectrum of polyester from fumaric acid

Chemical shift δ (ppm)	Assignment	
7.15	meta proton	[H^B]
6.85	ortho proton	[H^A]
4.20	>−O−C−CH−O− (with C above CH)	[H^C]
3.90	>−O−C−C−O− (with H and C above)	[H^D]
3.75	>−O−C−C−O− (with C above, H below)	[H^E]
1.65	C−C−C with CH$_3$ above and CH$_3$ below	[H^F]
1.30	>−O−C−C−O−C−C=C−C− with CH$_3$, O above	[H^G]

The ^{1}H-NMR spectrum of polyester from maleic anhydride (Figure 4.10) was shown the signal of methyl proton that would be experiment differently in NMR. Therefore they appeared at difference chemical shift, 1.40 and 1.25 ppm. Consequently, the ^{1}H-NMR spectrum maleic anhydride confirmed that it has a mixture of cis- and trans-isomer of carbonyl group. Percent of cis- and

trans-isomer of carbonyl group can be calculated from the height of signals, as folows :

% of carbonyl group in cis-form $\quad = \dfrac{M}{M + F} \times 100 = 42\%$

% of carbonyl group in trans-isomer $= \dfrac{F}{M + F} \times 100 = 58\%$

where : M = the height of signal of methyl proton in cis-isomer

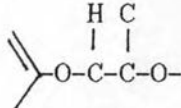F = the height of signal of methyl proton in trans-form
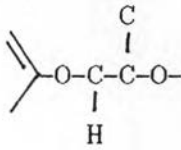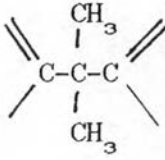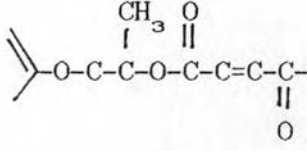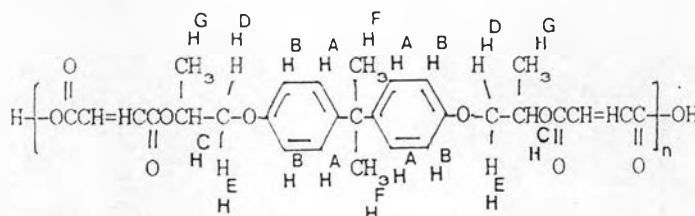
polyester from maleic anhydride
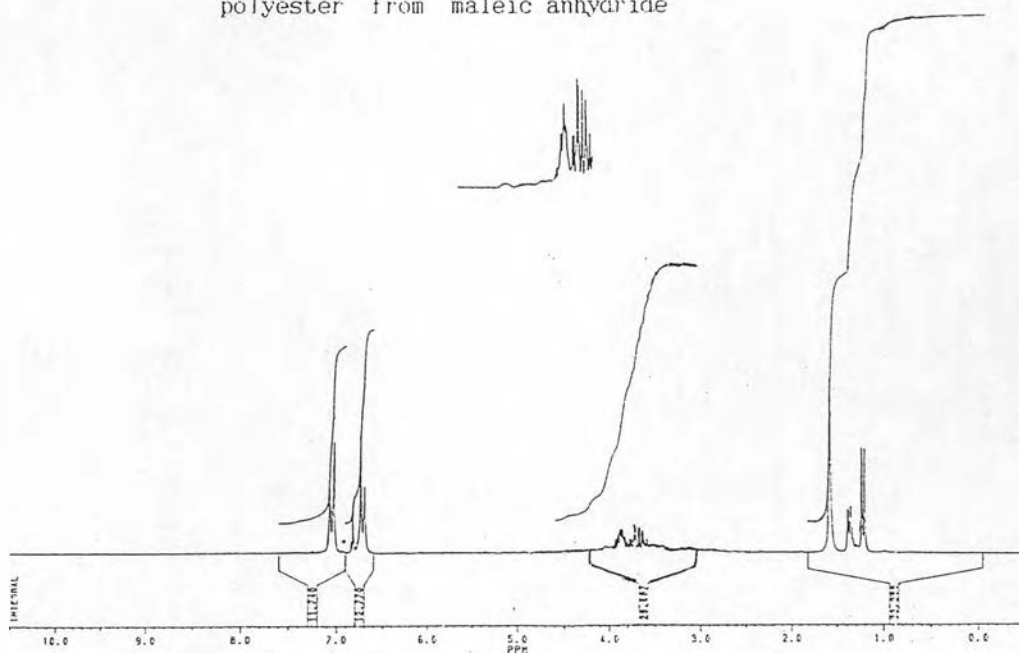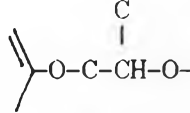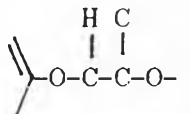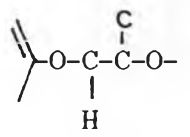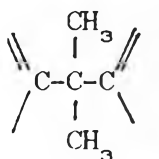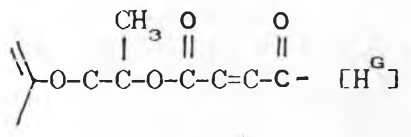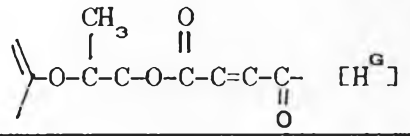
Figure 4.11 ^{1}H-NMR (CDCl$_3$) spectrum of polyester from maleic anhydride

Table 4.8 The assignment for the ^{1}H-NMR spectrum of polyester from maleic anhydride

Chemical shift δ (ppm)	Assignment
7.15	meta proton [H^B]
6.80	ortho proton [H^A]
4.10	$\overset{\displaystyle C}{\underset{}{\text{O-C-CH-O-}}}$ [H^C]
3.80	$\overset{\displaystyle H\ C}{\underset{}{\text{O-C-C-O-}}}$ [H^D]
3.65	$\overset{\displaystyle C}{\underset{\displaystyle H}{\text{O-C-C-O-}}}$ [H^E]
1.60	$\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\text{C-C-C}}}$ [H^F]
1.40	$\overset{\displaystyle CH_3\ O\quad\ O}{\underset{}{\text{O-C-C-O-C-C=C-C-}}}$ [H^G]
1.25	$\overset{\displaystyle CH_3\ O}{\underset{\displaystyle O}{\text{O-C-C-O-C-C=C-C-}}}$ [H^G]

Both of the unsaturated polyester resins have similar thermogram characteristic. The glass transition temperature were about 139°C for polyester from fumaric acid and 137°C for polyester from maleic anhydride. These results from polyester

from fumaric acid has carbonyl groups in trans-isomer (100%) along the chain, syndiotactic polymer, the polyester chain was more rigid thus it must use more energy to deform. While polyester from maleic anhydride has carbonyl groups as mixture of cis- and trans-isomers, atactic polymer, the chain was more flexible and easy to deform. They did not have melting temperature but decomposed at 300°C (see Figure 4.12).
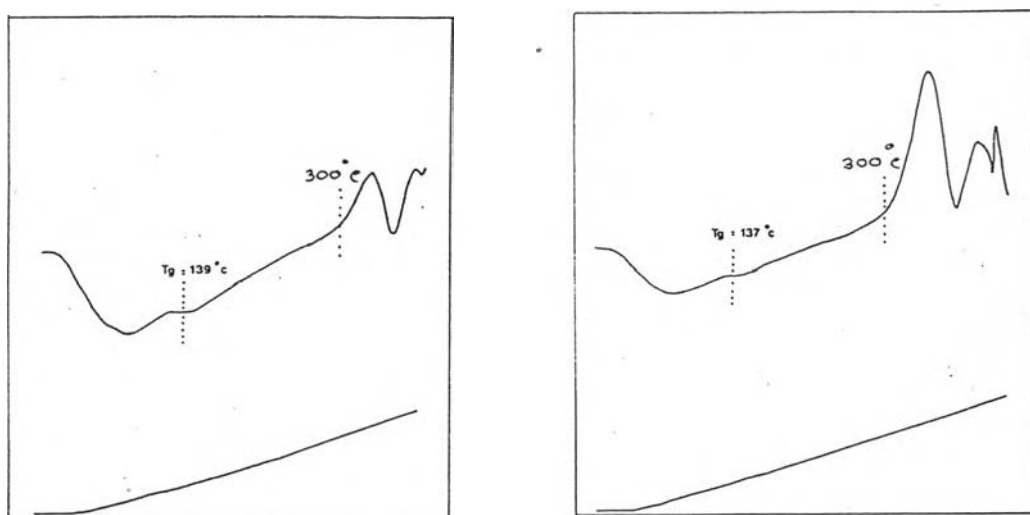
(A) : fumaric acid polyester   (B) : maleic anhydride polyester

Figure 4.12 Differential thermal analysis thermograms
of both unsaturated polyester resins

4.3 Preparation of an Oil-in-water Type Emulsion of the Unsaturated Polyester Resins

The emulsification of oil or hydrophobic materials with water can be divided into two types, one as water-in-oil (w/o) emulsion, two as oil-in-water (o/w) emulsion. The relative simultaneous attraction of an emulsifier for water and for oil or for the two phases of the emulsion system being considered

is known as the "Hydrophile-lipophile balance (HLB)". It is determined by the chemical composition and extent to ionization of a given emulsifier. The HLB of an emulsifier determines the type of an emulsion that tends to be formed. Thus emulsifiers with low HLB values tend to make w/o emulsions. The most stable emulsion systems usually consist of emulsifying agent that one portion having lipophilic tendency (low HLB value), the other portion having hydrophilic tendency (high HLB value). By blending two emulsifiers, the exact HLB needed can be attained rather than trying a single emulsifier having an HLB that does not quite match (47,48). In this experiment the present system is an oil-in-water emulsion in which the oil is the dispersed phase (internal phase) in water as the continuous phase (external phase). Therefore, a special surfactant was added into the system to help polyethylene glycol (HLB 6.0) stabilize o/w emulsion.

Preparation of oil-in-water type emulsion can be done by three methods (49) :

1. The surfactant is added to the water, and then oil is added slowly with agitation. This produces an o/w emulsion directly.

2. The emulsifying agent is dissolved in the oil phase, thus this mixture is added directly to water forming an o/w emulsion.

3. When the water is added to the oil surfactant mixture, a w/o emulsion is formed first which inverts to an o/w emulsion. This method produces exceedingly fine particle size emulsion. Viscosity is at its maximum value at the inversion point (see Figure 4.13).
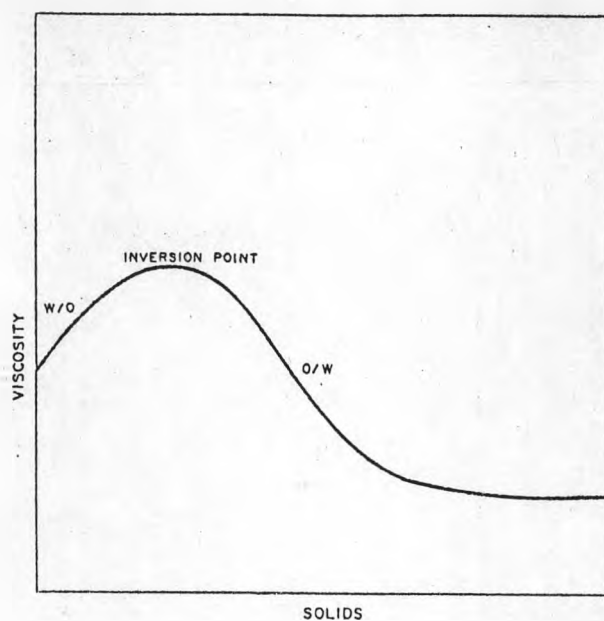
Figure 4.13   Inversion of an emulsion

To   prepare this emulsion, the aqueous phase   is   stirred
into the oil phase containing the emulsifying agents. The aqueous
phase   has   to   be   introduced   carefully,   possibly   portionwise,
because   it   has been found that   in   the   case   of   more   highly
viscous   oil   phase,   mechanical difficulties   are encountered in
incorporating   the   aqueous   phase owing   to the   fact that   with
increasing   viscosity of the   reverse emulsion, the aqueous phase
is   taken up   more and   more slowly. As   more water is added, the
emulsion assumes a milky cast   while the viscosity increases.   At
a certain   point,   called   the   inversion   point,   the   viscosity
suddenly   decreases.   At this   point   the   emulsion   has   changed
from w/o to o/w. Further addition of   water may then   be rapidly.
Finally,   the   protective   colloid   agent   which   normally   is
poly(vinyl   alcohol)   as water soluble   hydrophilic   colloid   was
added   to   the   emulsion   dispersed   in   water   phase to   protect

coagulation and setting of emulsion. This o/w type emulsion appears as milky-white emulsion. Emulsion has to be kept tightly to avoid loss of water. Water loss may effect emulsion instability and result in phase separation. After prolonged storage, the emulsion may become creaming or sedimentation. If no coalescence or agglomeration occurs, the emulsion may be redispersed, a shake-well before using it, and provide a satisfactory product.

The difference of two emulsion system, one with fumaric acid and the other with maleic anhydride, is the color of emulsion. The oil-in-water type emulsion of unsaturated polyester resin that has fumaric acid was milky-white color and it has stability about 30 days at room temperature, but that has maleic anhydride was milky-yellow color and it has stability about 7 days at room temperatore. Both of the emulsion should not be kept in refrigerator or at higher temperature because their characteristic will be changed which will cause the loss of the stability faster than they should be.

4.4 Preparation of Sizing Agents

Theoretically, the sizing agent consist of six compositions, i.e., film-forming agent, coupling agent, antistatic agent, lubricant, pH controller and water. Each composition has important role in making glass fiber reinforced plastic. The sizing agent may also modify the interface region to strengthen the organic and inorganic boundary layers (36) as can be seen in Figure 4.14.

Reinforcement
Interface
Matrix
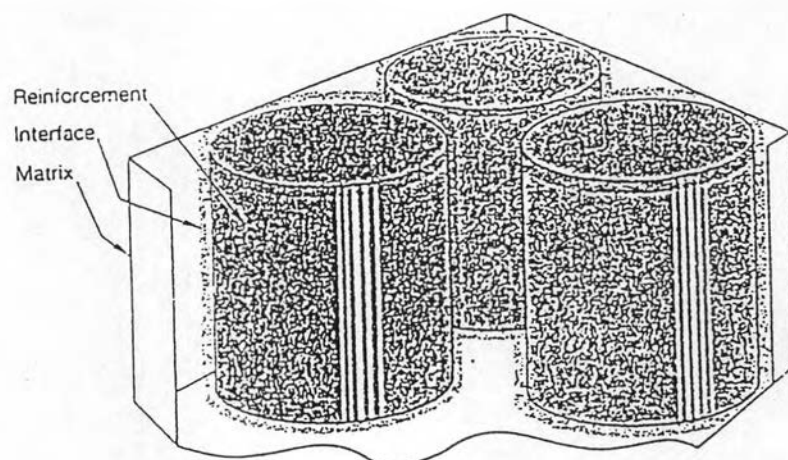
Figure 4.14 The model structure showing the boundary of
interface layer between the surface of
matrix and the glass fiber

In this experiment, it will be specifically focussed at
film-forming agent. In the past, poly(vinyl acetate) was used as
film-forming agent. But at the present, the polymer that is the
same as the polymer matrix in glass fiber reinforced plastic is
preferably. selected to use as film-forming agent. Owing to their
similarity which make them well-link to each other, the high
performance fiberglass products would be produced. From this
reason, the unsaturated polyester was selected to use as
film-forming agent in this experiment.

In this research work, two polyester formula were
synthesized, one from fumaric acid and the other from maleic
anhydride by control the other components. Both polyesters have
similarly structure but fumaric acid gives lighter-colored
product than maleic anhydride. Then they were used to prepare

an oil-in-water type polyester emulsion as film-forming agents. The polyester emulsion from fumaric acid has white-color, but the polyester emulsion from maleic anhydride has yellow-color. This type of unsaturated polyester from fumaric acid was used as film-forming agent in some sizing agent which showed that it improved transparency of glass fiber reinforced polyester (7,8). However, there has been report about the effect of this unsaturated polyester on the transparency and strength of the fiberglass products. From these reasons, both polyesters were used in the sizing agents which were prepared in seventeen formulations as shown in Table 4.8.

4.5 Glass Fiber Manufacturing

Production of continuous filament fibers proceeeds by feeding the raw glass into an electrically heated fiberizing element at 2300°F or 1260°C, referred to as bushing. At the bottom of the bushing there are a large number of orifices. The droplets of molten glass extruding from each orifice are gathered together, mechanically attenuated to the proper dimensions, passed through a light water spray (quench) and passed a sizing applicator. The filaments are then gathered together in a suitably shaped shoe to from a bundle of filaments called a strand. The strand passes to a winder where it is wound onto a forming tube (Figure 4.15). The strand material so formed is frequently referred to as a forming cake (Figure 4.16). The wet cake is determined moisture content and sizing agent content. The cake is then conditioned or dried in oven at 120°C about 14 hours prior to further processing into sallable products. The dried cake is determined moisture content again to check for the residual moisture content.

GLASS FEED...Raw Glass Components or Marbles

GLASS MELT...Molten Glass

MELTING FURNACE AND FIBERIZING ELEMENT

Protective Coating Applications...SIZING

Strand Forming...GATHERING

.....Strand

.....Strand on Forming Tube

WINDING

SOLVENT REMOVAL OR DRYING

Strand on Forming Tube

ROVING FABRICATION

CREEL

....Strands

WINDING...Roving Package

YARN FABRICATION

UNWINDING...Strand on Forming Tube

TWISTING...Yarn on Twister Tube (and plying)

Figure 4.15   The glass fiber manufacturing process

Figure 4.16   Glass fiber forming cake

Practically, the droplets of molten glass are extruded from about 800 orifices. Then the filaments are gathered together by a 16 bar shoe to make proper dimension which is appropriate with the chopped strand fiber. The placement of the filaments into every bar of shoe is very difficult technique. Generally, they are placed into shoe about 14-16 bar depending on the skilled labor. The received glass fibers have splitting efficiency equal to 8 and 11 strand as shown in Table 4.8. The sizing agent also has effect on the splitting efficiency of the glass fibers. If it uniformly coats on the filaments surface, the recieved glass fibers will have splitting efficiency equal to the number of the strand that passes through suitably shaped shoe. Seeing one strand by naked eye, it was difficult to explain that in one strand was composed of many filaments. The using of the high quality color video microscope system can illustrated as in Figure 4.17.

CHULALONGKORN UNIVERSITY: GLASS FIBER NO. 12

Figure 4.17 Magnification of a strand of glass fiber
(250X)

Table 4.8 Specifications of the glass fibers

Sizing agent formulation	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Polyester emulsion (50% solid), %																	
- Fumaric acid	-	0.50	0.50	-	-	2.50	2.50	-	-	3.50	3.50	-	-	5.00	5.00		
- Maleic anhydride	-	-	-	0.50	0.50	-	-	2.50	2.50	-	-	3.50	3.50	-	-	5.00	5.00
Poly(vinyl acetate) emulsion (50% solid), %	5.00	-	5.00	-	5.00	-	0.50	-	5.00	-	5.00	-	5.00	-	5.00	-	5.00
Coupling agent, %	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Antistatic agent, %	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Lubricant, %	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Acetic acid	little	little	little	little	little	little	little	little	little	little	little	little	little	little	little	little	little
Deionized water	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Solids content of sizing agent, %	3.4371	1.0588	3.0853	0.9642	3.1649	2.1199	4.9769	2.1695	5.1134	4.6722	5.1703	4.9083	5.2474	5.1734	9.0724	6.6613	9.1217
Moisture content of wet cake, %	10.0065	13.0389	9.6623	12.3497	11.9600	12.3371	11.1633	13.4110	12.0140	11.2398	10.1102	12.1224	8.9615	11.7359	11.0102	10.5836	10.8004
Sizing agent content on glass fiber, %	0.8368	0.1960	0.8546	0.1939	0.7983	0.3723	1.1320	0.3708	1.1234	0.4674	1.0172	0.4988	1.0620	0.5054	1.2290	0.6167	1.1748
Glass fiber color	white	white	white	white	white	white	white	white	white	white	white	white	white	white	white	white	white
Glass fiber characteristics	very hard	soft	moderate hard	soft	moderate hard	moderate hard	hard	moderate hard	hard	moderate hard	hard	moderate hard	hard	moderate hard	hard	moderate hard	hard
	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle	no brittle
Splitting efficiency of glass fiber	8	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11

4.6 Lamination of the Glass Fibers and The Unsaturated Polyester
     Resins, ALPOLIT VUP 9026

Hand lay-up is the fabrication process that used in this
research. Owing to the glass fibers are in the chopped strand
form (2 inch length), thus they have several problem during the
lamination. The chopped strand fibers should be uniformly
dispersed throughout the lamination area to control the thickness
and the property of the laminate. The resin-glass mixture must
be rolled to squeeze the polyester resin into the glass strands
to ensure that the glass fiber are completely wetted by the resin
and to remove trapped air before cure (25). Practically, the air
bubbles should not appear in the laminate because they are the
starting point of cracking. Furthermore, when the laminating
roller is rolled on the laminate, some of the fibers can be
attached to the thread of the roller. Considerable operator skill
is thus needed in this fabrication. In other words, the quality
of the products depends on the skill of the personnel in removing
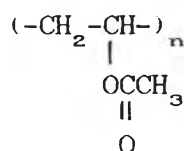air and voids.

ALPOLIT VUP 9026 is a medium viscous polyester resin.
Although crosslinking density through the unsaturated acids is
theoretically possible, the resulting three dimensional matrix
does not exhibit favorable properties. If, however, certain
unsaturated monomers such as styrene are used, both the rate
of reaction and the degree of crosslinking will markedly be
increased. In addition, the resulting crosslinked product has
greatly improved in the property (24). The crosslinking agent
also reduces viscosity of the resin cause the easy flow through
the glass fiber at the time of molding. Styrene and MMA were
chosen to comparatively study their effect to properties of the

properties of the laminates. The catalyst and the accelerator were used in smaller quantity than that assigned in Appendix A to adjust appropriate gelation time (about 30 minutes) for increased facilitation of this lamination.
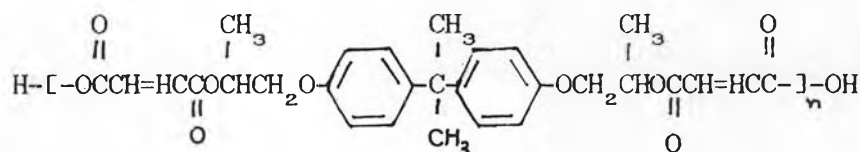
4.7 Effect of the Sizing Agents on Glass Fiber Characteristics

As exhibited in Table 4.8. All glass fibers have white-colored, but characteristics and splitting efficiency of each glass fiber was different due to the type and percent of film-forming agent in the sizing agents. Because of the sizing agents were prepared in water-based form, thus the film-forming agents must be prepared in emulsion form with water. The main structure of triple film-forming agent were shown as belows :

1. PVAc emulsion :

$$(-CH_2-CH-)_n$$
$$|$$
$$OCCH_3$$
$$\overset{\|}{O}$$

2. Polyester emulsion from fumaric acid :

$$H-[-OCCH=HCCOCHCH_2O-\langle\rangle-\overset{CH_3}{\underset{CH_3}{C}}-\langle\rangle-OCH_2CHOCCH=HCC-]_n-OH$$

3. Polyester emulsion from maleic anhydride :

$$H-[-OCCH=CHCOCHCH_2O-\langle\rangle-\overset{CH_3}{\underset{CH_3}{C}}-\langle\rangle-OCH_2CHOCCH=HCC-]_n-OH$$
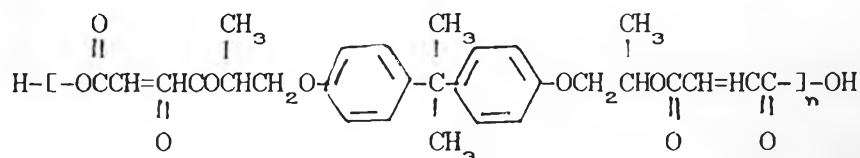
Poly(vinyl acetate) is an atactic polymer which does not have crystallinity in molecule. The functional group $-O\overset{O}{\overset{||}{C}}CH_3-$ is a bulky group, thus the polymer chain has low flexibility. When poly(vinyl acetate) is used as film-forming agent on glass fiber surface, it will produce very hard glass fiber.

The polyester has two phenyl groups (-⟨benzene ring⟩-) that make the chain rigid, but the other functional group as $-O-$, $-\overset{O}{\overset{||}{C}}-O-$ and $-CH=CH-$, will increase the flexibility of chain. The 0.5 % by weight of both polyester emulsion will produce soft glass fiber. The increase of percent of both polyester emulsion to 2.5, 3.5 and 5.0 % by weight will moderately increase the hardness of glass fiber. This can be explained that phenyl groups have more effect than the other functional groups. Industrially, the soft glass fiber is not appropriate for using in chopped strand mat machine because it is very difficult to cut to the desired size. Thus 5.0 % by weight of PVAc emulsion was mixed with both polyester emulsion for adjusting the hardness of glass fiber. The functional group $-O\overset{O}{\overset{||}{C}}CH_3-$, in PVAc and the phenyl groups in polyesters will concomitant in promotion of the hardness glass fiber.

4.8 Effect of the Sizing Agents and the Crosslinking Agents on Transparency of the laminates

The transparency of the laminates depends on the sizing agent on glass fiber surface and the crosslinking agent added to the polyester resin. Theoretically, if the refractive index of glass fiber is equal to the one of polyester resin, the laminate will have high transparency. Normally, E-glass has refractive index about 1.547. When it is treated with the sizing agent, its

refractive index is slightly changed. The crosslinking agent also has effect to the refractive index of polyester resin.

The transparency of the laminate can be determined as percent light transmission of the laminate. The results of light transmission of the laminates when percent of triple film-forming agent and dual crosslinking agent were varied in different types were shown in Table 4.9.

Figure 4.18-4.19 showed the light transmission of the laminates in which of both polyester emulsion were varied, i.e., 0.5, 2.5, 3.5, and 5.0%. It exhibited that either styrene or methyl methacrylate as crosslinking agent was used, the results were very similar even though in case of methyl methacrylate, it seemed a little better than styrene (Figure 4.20). This was expected that the polyester resin containing methyl methacrylate would have the refractive index closer to glass fiber that coated with both polyester emulsions than the one with styrene. PVAc emulsion was given very low light transmission because of it can not well-link with the unsaturated polyester resin (ALPOLIT VUP 9026). For the polyester emulsion from fumaric acid using 0.5% by weight and 5.0% PVAc emulsion, it was noted that the light transmission was quite low in both cases containing either styrene or methyl methacrylate. This probably due to this glass fiber has refractive index farther from polyester resin containing both crosslinking agent.

Accelerators that mixed with polyester resin has effect to transparency of the laminates. Stable solutions of cobalt octoate in dimethyl phthalate are possible and these are often prefered because they impart less color to the laminates.

Table 4.9 Effect of percent of triple film-forming agent and
dual crosslinking agent on light transmission of
the laminates

Percent of film-forming agent			Crosslinking agent			
Poly(vinyl acetate) emulsion	Fumaric acid polyester emulsion	Maleic anhydride polyester emulsion	Styrene Light transmission		Methyl methacrylate Light transmission	
(50% solid)	(50% solid)	(50% solid)	$\overline{X}_{LT}$ (%)	Std.dev	$\overline{X}_{LT}$ (%)	Std.dev
5.00	-	-	74.23	4.30	80.19	3.14
-	0.50	-	86.98	1.53	86.46	1.33
5.00	0.50	-	80.31	2.26	81.23	2.22
-	-	0.50	87.31	1.46	88.08	1.30
5.00	-	0.50	85.04	0.92	86.20	1.62
-	2.50	-	87.53	1.54	87.68	0.90
5.00	2.50	-	86.22	2.81	86.64	1.62
-	-	2.50	86.58	2.83	87.73	1.23
5.00	-	2.50	85.97	1.33	86.63	1.48
-	3.50	-	85.67	0.71	87.07	1.30
5.00	3.50	-	86.32	1.81	86.75	1.73
-	-	3.50	85.46	1.69	85.95	1.22
5.00	-	3.50	85.63	1.24	85.70	1.67
-	5.00	-	87.36	1.49	87.06	1.61
5.00	5.00	-	86.53	1.65	87.04	1.74
-	-	5.00	87.48	1.26	86.78	1.57
5.00	-	5.00	85.11	1.36	85.79	1.77

Note : $\overline{X}_{LT}$ stand for an average value of light transmission for
30 measurements.

Light transmission (%)

Percent of polyester emulsion (Styrene)

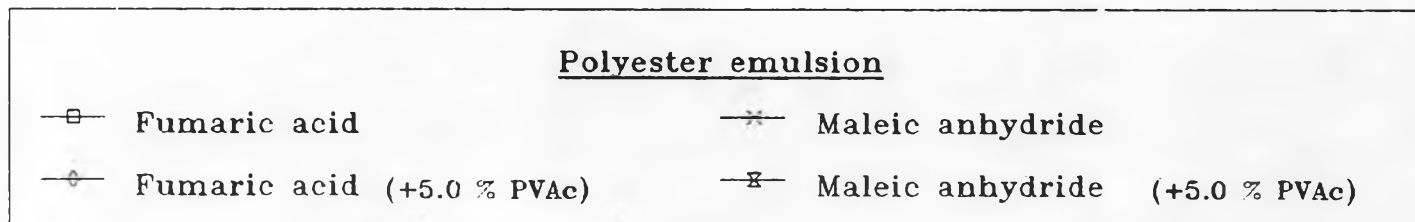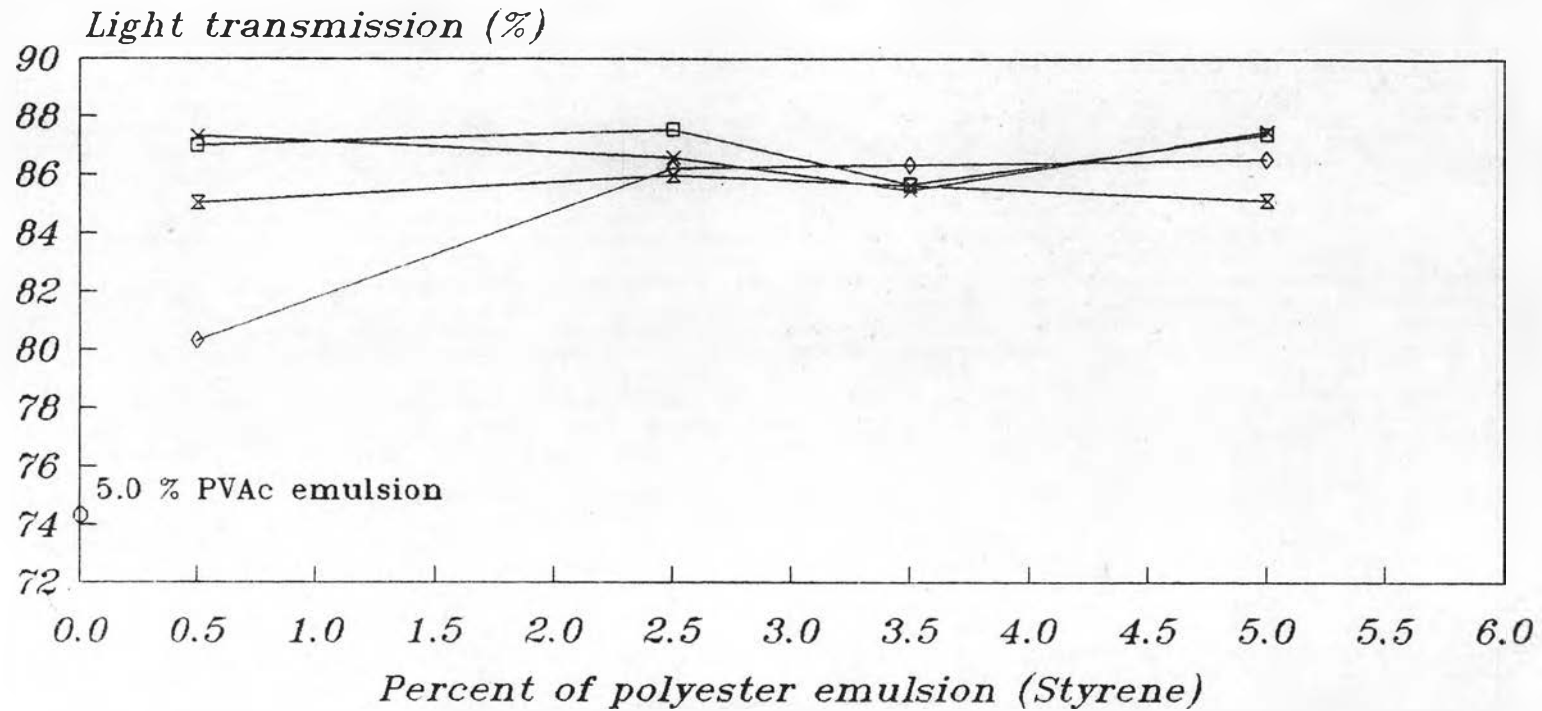| Polyester emulsion	
—□— Fumaric acid	—※— Maleic anhydride
—◇— Fumaric acid (+5.0 % PVAc)	—☒— Maleic anhydride (+5.0 % PVAc)

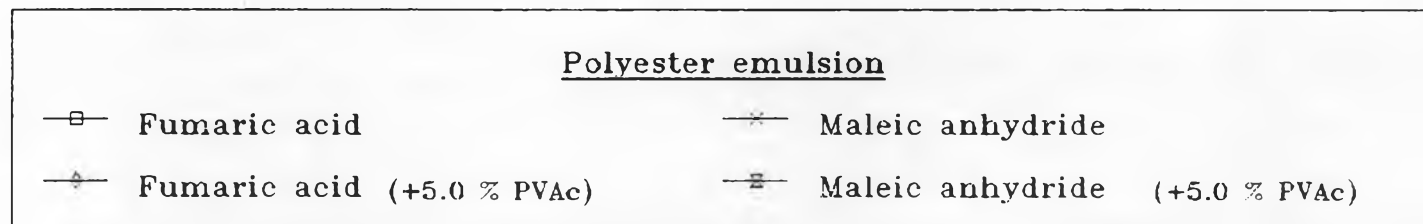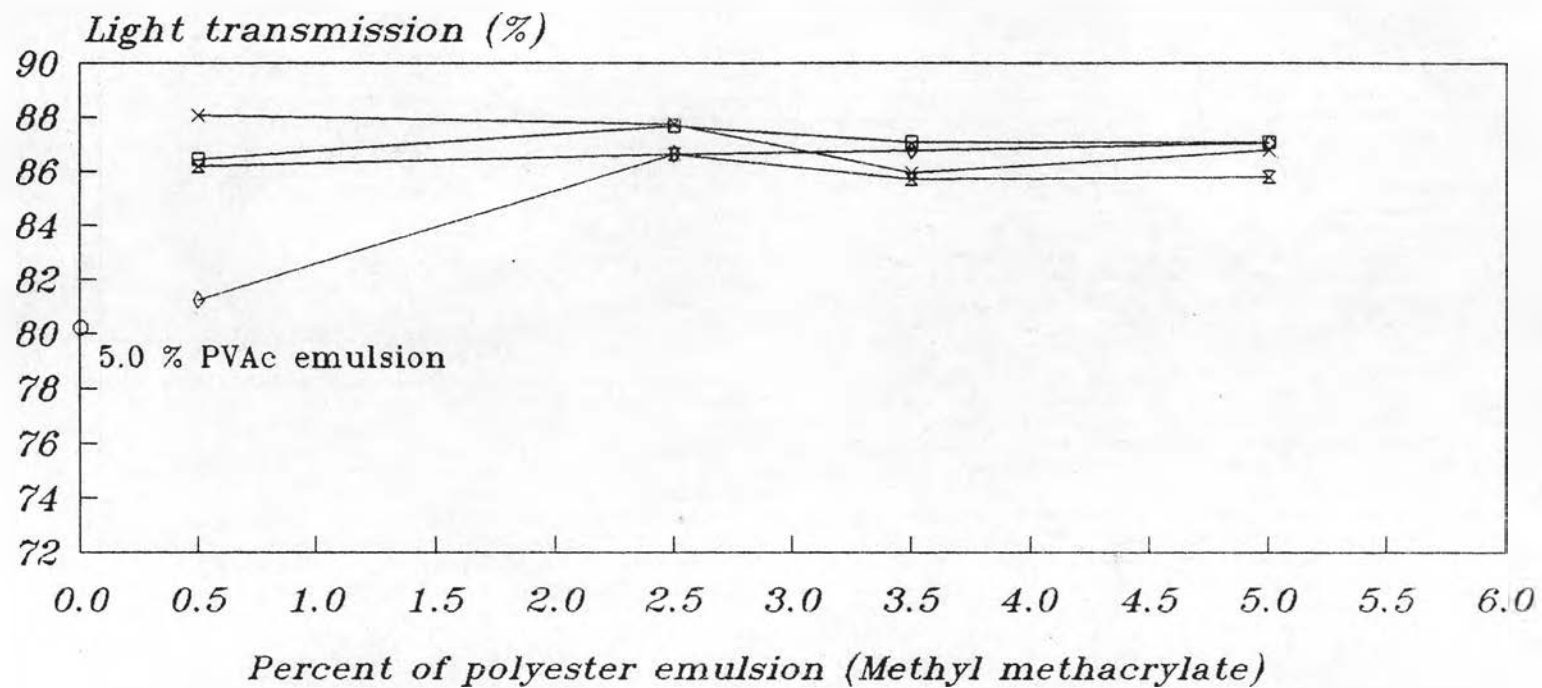**Figure 4.18** Light transmission of the laminates using styrene as crosslinking agent.

Figure 4.19 Light transmission of the laminates using methyl methacrylate as crosslinking agent

Light transmission (%)

90
88
86
84
82
80
78
76
74
72

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0

Percent of fumaric acid polyester emulsion

–□– Styrene   –×– Methyl methacrylate

Light transmission (%)

90
88
86
84
82
80
78
76
74
72

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0

Percent of maleic anhydride polyester emulsion

–□– Styrene   –×– Methyl methacrylate

Light transmission (%)

90
88
86
84
82
80
78
76
74
72

5.0 % PVAc emulsion (methyl methacrylate)

5.0 % PVAc emulsion (styrene)

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0

Percent of fumaric acid polyester emulsion
(+5.0 % Polyvinyl acetate emulsion)

–□– Styrene   –×– Methyl methacrylate

Light transmission (%)

90
88
86
84
82
80
78
76
74
72

5.0 % PVAc emulsion (methyl methacrylate)

5.0 % PVAc emulsion (styrene)

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0

Percent of maleic anhydride polyester emulsion
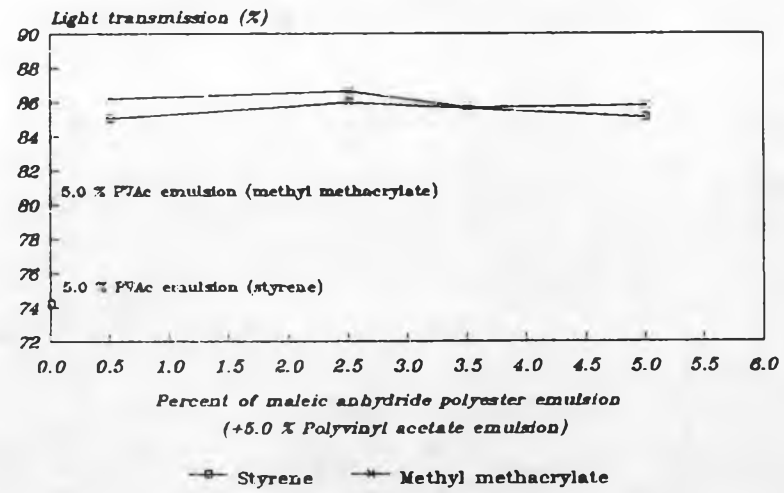(+5.0 % Polyvinyl acetate emulsion)

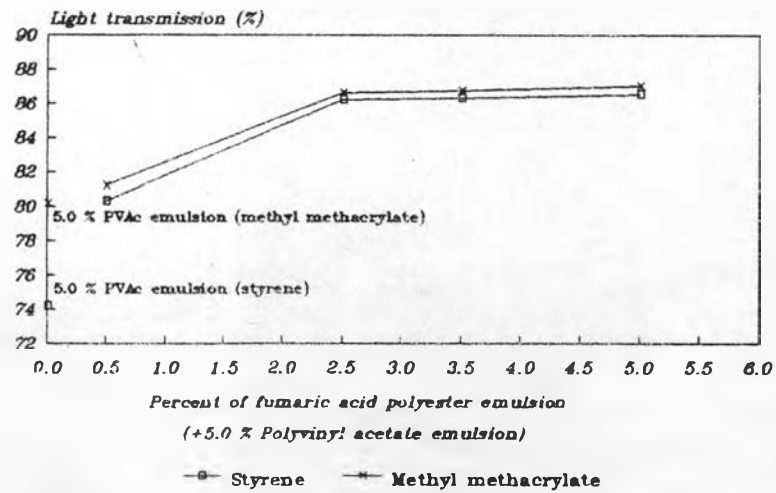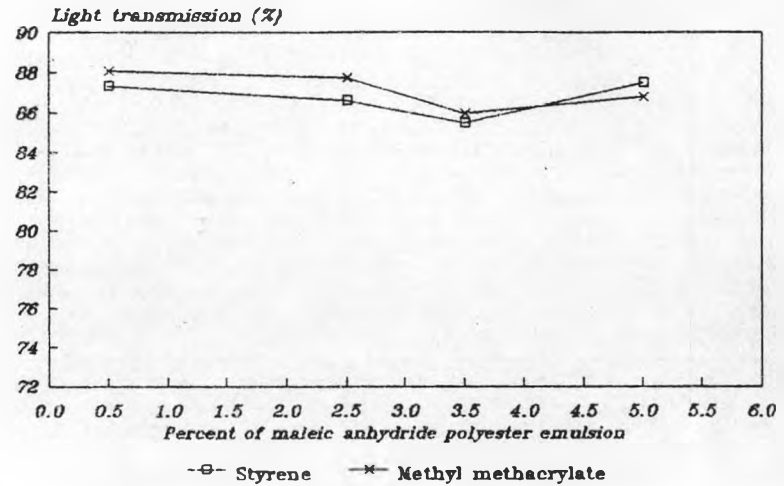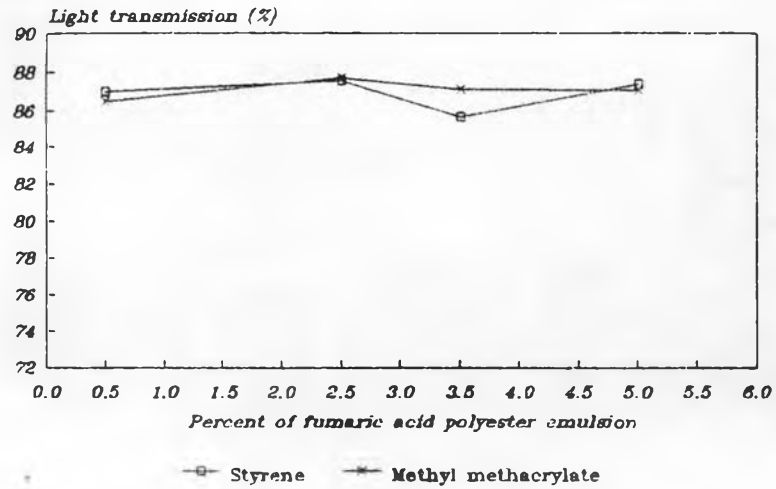–□– Styrene   –×– Methyl methacrylate

Figure 4.20 The comparison of light transmission of the laminates using
dual crosslinking agent (styrene and methyl methacrylate)

Mylar film that used as mold releasing agent in the lamination should have smoothly and cleanly surface and the appropriate thickness of mylar film also has greatly effect to the smoothly surface and transparency of the laminates.

4.9 Effect of the Sizing Agents and the Crosslinking Agents on Mechanical Properties of the laminates

Mechanical properties of the laminates depend primarily on combined effect of amount of glass fiber reinforcement and arrangement of glass strand in finished product (19). As shown by the straight line graph of Figure 4.21. As regards the resin-to-glass ratio, the glass fiber is much stronger than the resin, so logically, the high proportion of glass fiber in composite is, the greater the strength and modulus are. 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.

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 strength and modulus of composites will be reduced when the fibers are not parallel to the loading direction. In this experiment, the chopped strand glass fibers are randomly oriented in the laminate. Therefore, the properties of a chopped strand fiber reinforced composite can be isotropic; that is, the properties do not change with direction within the plane of the laminate. Although the strength is equal in all directions, but it is smallest when compared with other arrangement.
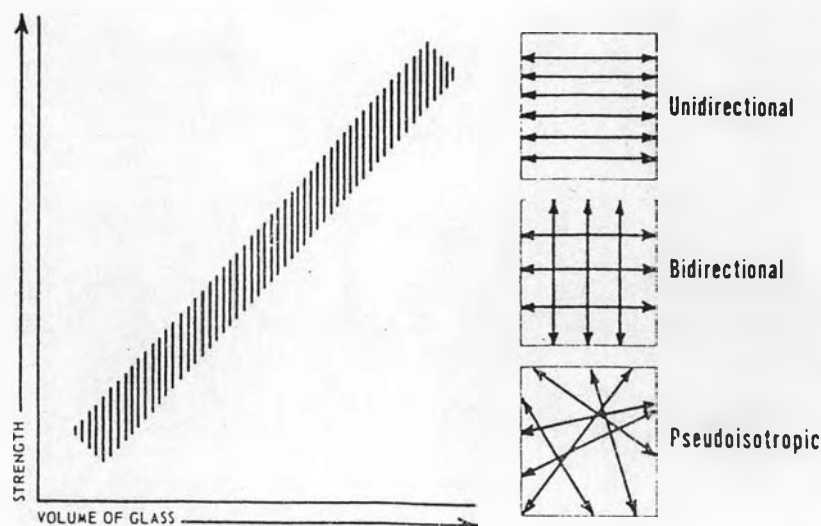
Figure 4.21 Relationship of strength to glass volume and
reinforcement arrangement

For the effect of glass fibers on the strength of the
laminates, there are two possible causes for this variable :

1. it can occur as a result of variations in the fiber
length with diameter from the manufacturing process.

2. it can occur as a result of handing facility of
fibers and from their surface treatment because of differences in
the nature and intensity of chemical reaction at the
coating-fiber interface.

Continuous glass fibers normally have higher strength
than chopped strand fibers. Although fibers of greater diameter
can add and have been made, they have reduced flexibility and
begin to assume the properties of the counterpart bulk material.
In other words, with increased diameter they perform more as rods
rather than as fibers.

Chopped strand glass fibers are available with different sizing agents for compatibility with most plastics. Furthermore, the sizing agents have greatly influence to the curing behavior of polyester resin and consequently the mechanical and physical properties of laminated products. The silane coupling agents participate in the curing reaction of polyester resin, namely at the surface of the resin matrix, forming an interface bond of the glass fiber to resin. The interfacial bond between the matrix and the fibers is an important factor influencing the mechanical properties and performance of the laminates. The interface is responsible for transmitting the load from the resin to the fibers, which contributes to the greater strength of the laminates. 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 the length (38). Such a situation is well explained by the model of microcracking in Figure 4.22.
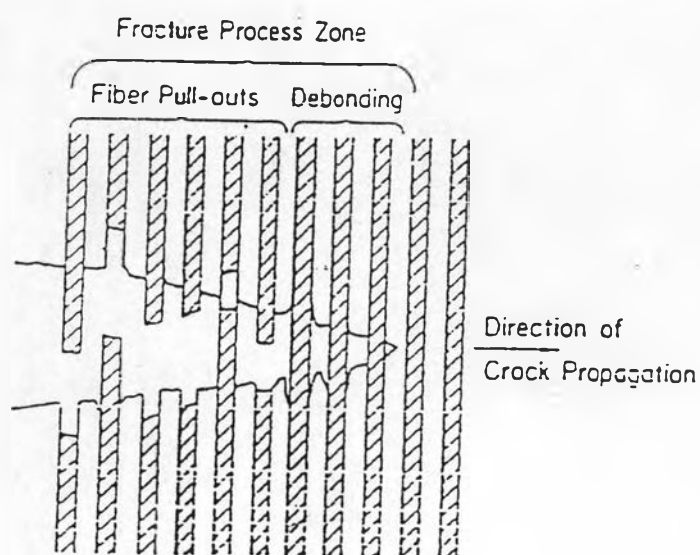

Figure 4.22 Model of microcrack tip in the fiber composites

In this study, test specimens were prepared from the formulation in Table 3.2 and subjected to the test methods of ASTM D790 mentioned previously. The results of mechanical properties of the laminates in which percent of triple film-forming agent and dual crosslinking agent were varied in different types were shown in Table 4.10.

The stress-strain curves for general hypothetical plastic materials are shown in Figure 4.23 (50) and the experiment result shows in Figure 4.24. It is generally observed that the laminates were hard and strong composites, thus they have high modulus, high yield stress, and high breaking stress and perhaps a moderate elongation at break.
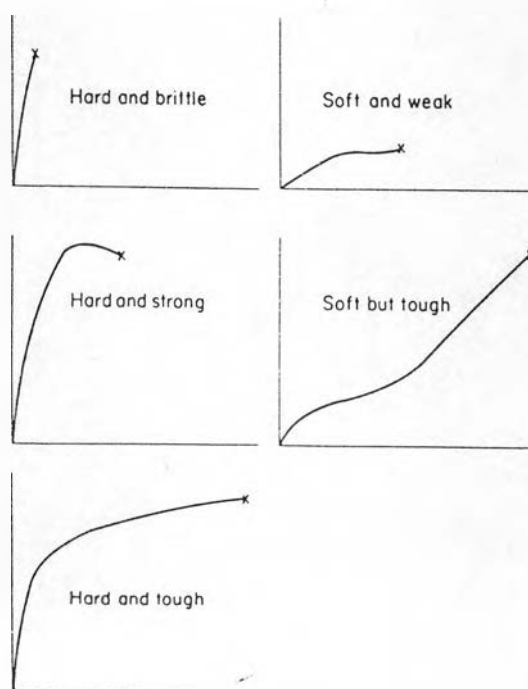

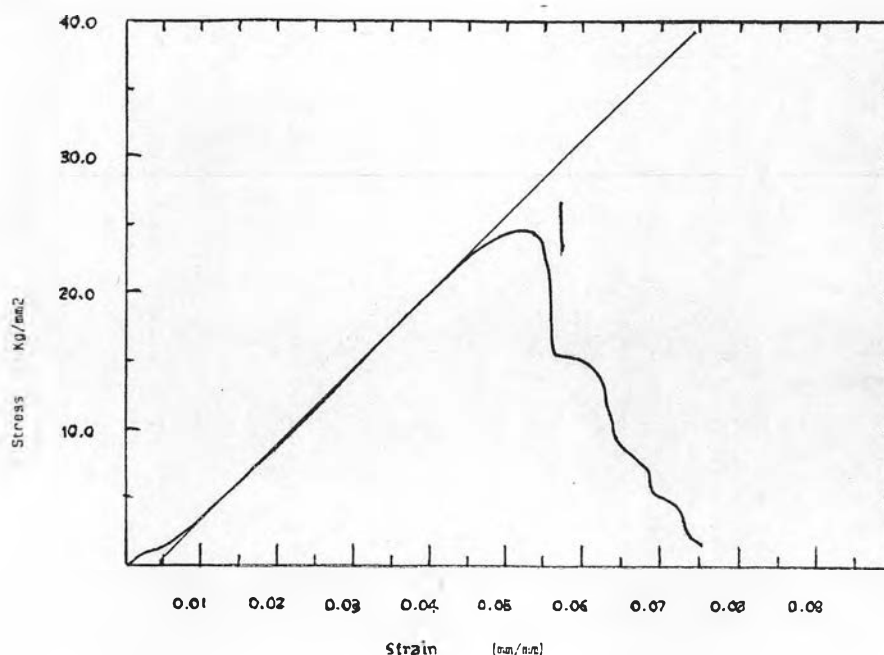Figure 4.23 Types of stress-strain curves

Figure 4.24 Stress-strain curve of the laminates

Figure 4.25-4.26 show the comparative flexural and modulus of the laminates in which percent of both polyester emulsion were varied, i.e., 0.5, 2.5, 3.5, and 5.0% and styrene was used as crosslinking agent. Polyester emulsion from fumaric acid has highest mechanical properties at 0.5%. However, the results were greatly decreased as percent of polyester emulsion from fumaric acid was increased to 2.5, 3.5, and 5.0%. This result from when the thickness of film-forming agent layer on glass fiber surface was increased, styrene can crosslinked between the double bond in polyester resin and only the upper layer of double bond in polyester emulsion from fumaric acid. Thus the polyester resin can not well-linked with the glass fibers as the percent of polyester emulsion from fumaric acid was increased.

The mechanical property of polyester emulsion from maleic anhydride was found to be better when percent of polyester

Table 4.10 Effect of percent of triple film-forming agent and dual crosslinking agent on mechanical properties of the laminates

Percent of film-forming agent			Crosslinking agent							
Poly(vinyl acetate) emulsion	Fumaric acid polyester emulsion	Maleic anhydride polyester emulsion	Styrene				Methyl methacrylate			
			Flexural strength		Flexural modulus		Flexural strength		Flexural modulus	
(50% solid)	(50% solid)	(50% solid)	$\bar{X}_{rs}$ (MPa)	Std.dev	$\bar{X}_{rm}$ (MPa)	Std.dev	$\bar{X}_{rs}$ (MPa)	Std.dev	$\bar{X}_{rm}$ (MPa)	Std.dev
5.00	-	-	206.41	38.03	6678.00	1281.22	215.51	47.08	7472.27	1382.27
-	0.50	-	236.29	37.74	8002.60	2048.30	205.58	47.03	7275.67	1392.64
5.00	0.50	-	233.01	43.52	6597.33	1348.92	217.20	46.88	7427.00	1384.31
-	-	0.50	208.99	38.22	7111.63	910.11	218.25	43.26	8051.48	1294.90
5.00	-	0.50	220.12	36.27	7347.10	724.09	200.48	40.78	7255.57	959.79
-	2.50	-	214.28	54.50	6716.36	918.90	219.99	37.93	7447.52	1149.58
5.00	2.50	-	212.42	40.77	6499.01	1079.17	212.95	40.28	7065.50	1354.40
-	-	2.50	225.91	35.17	7666.26	971.38	218.12	36.53	7783.51	990.63
5.00	-	2.50	221.07	36.27	7423.00	779.41	223.19	43.56	7848.40	1023.42
-	3.50	-	208.86	41.02	6616.50	902.09	210.40	41.79	7226.36	1158.73
5.00	3.50	-	204.88	44.34	6402.67	1190.21	221.33	31.14	7421.93	1160.67
-	-	3.50	234.10	40.27	8101.92	996.69	222.76	47.92	8001.71	1421.48
5.00	-	3.50	230.85	52.25	7551.56	1101.82	240.11	40.46	8202.22	999.19
-	5.00	-	195.58	49.03	6234.90	915.77	240.60	35.19	8155.28	1251.56
5.00	5.00	-	193.11	43.26	6011.05	920.02	235.81	43.22	7611.36	1163.61
-	-	5.00	204.64	28.35	6453.89	1000.74	249.66	38.35	9086.93	2749.70
5.00	-	5.00	196.63	31.63	5880.73	845.64	244.92	45.00	8316.08	1457.80

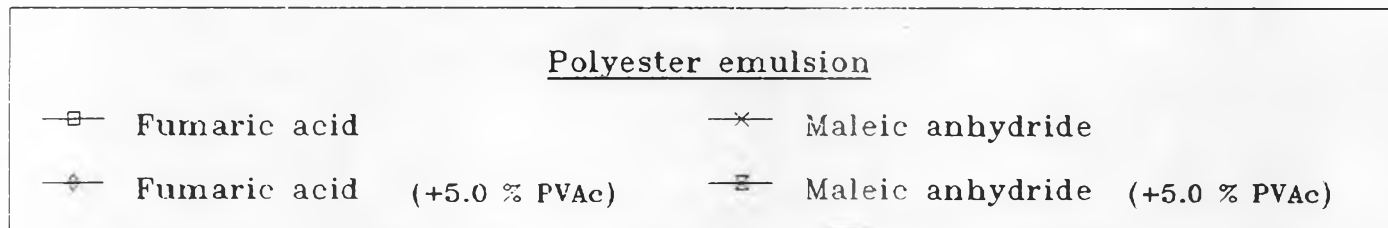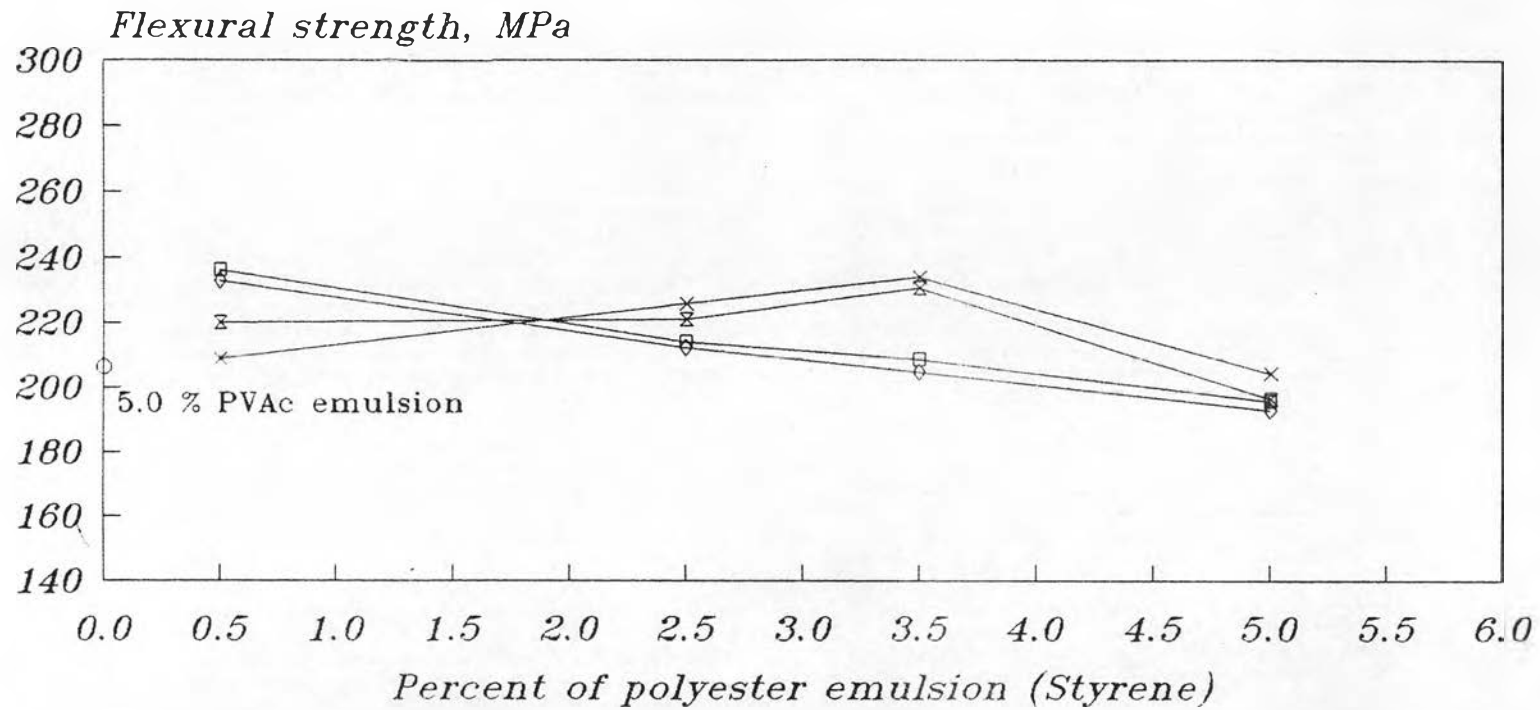Note : $\bar{X}_{LT}$ stand for an average value of light transmission for 30 measurements

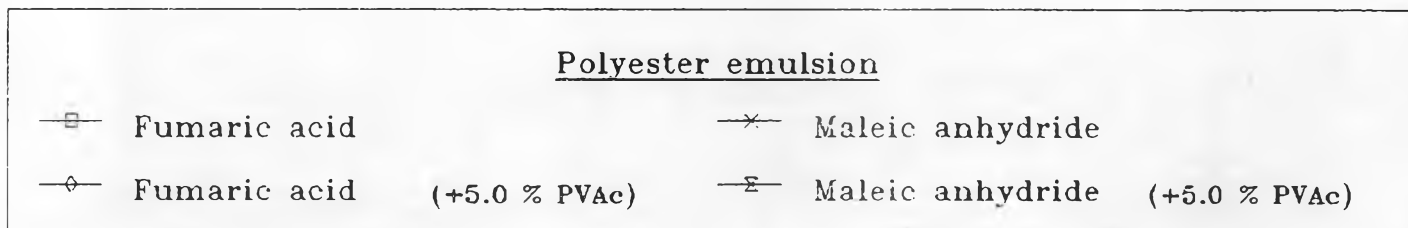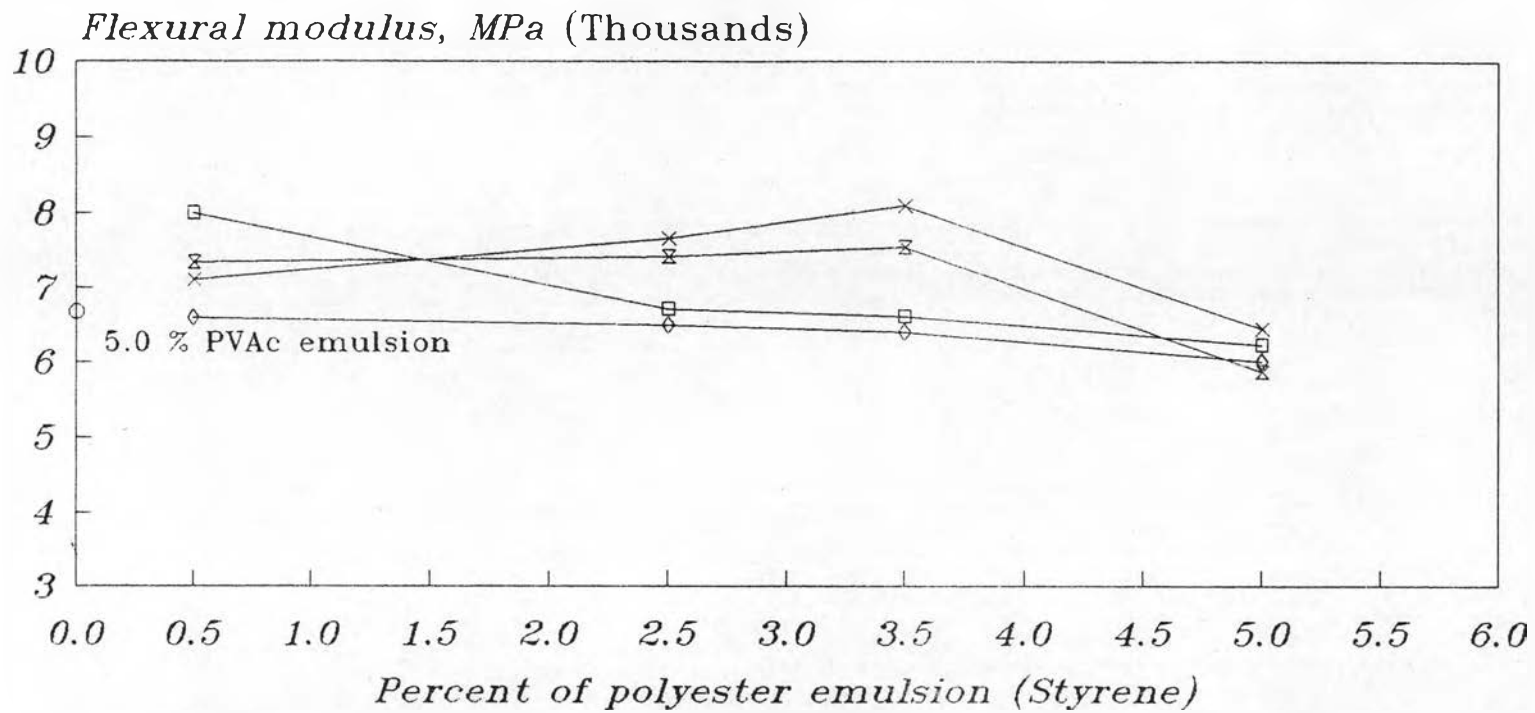Figure 4.25 Flexural strength of the laminates using styrene as crosslinking agent

Figure 4.26 Flexural modulus of the laminates using styrene as crosslinking agent.

emulsion from maleic anhydride was increased from 0.5 to 3.5%. Polyester emulsion from maleic anhydride has double bond in cis-form 42% along the chain which has lower reactivity with styrene. When percent of polyester emulsion from maleic anhydride was increased, the crosslinking between polyester resin and polyester emulsion was increased, thus the mechanical properties were increased. These results from when the thickness of film-forming agent was increased, styrene can flow through the layer of film-forming agent to crosslinked with the double bond of polyester emulsion from maleic anhydride in the inner layer. But the result was greatly decreased at 5.0% polyester emulsion from maleic anhydride because of the exceeding thickness of the film-forming agent layer.

Figure 4.28-4.29 show the comparative flexural strength and modulus of the laminates when percent of both polyester mulsion were varied from 0.5, 2.5, 3.5 and 5.0% and methyl methacrylate was used as crosslinking agent. Both polyester emulsions have highest mechanical properties at 5.0%. Owing to methyl methacrylate has crosslinking ability between double bond in polyester resin and in both polyester emulsions as not good as styrene. Thus, the results at 0.5% of both polyester emulsions were lowest. When percent of both polyester emulsions were increased, the double bond were increased too. Therefore, the chance that methyl methacrylate will linked between double bond in polyester resin and in both polyester emulsions were increased. Thus, the increment of crosslinked density will increased the mechanical properties of the laminates.

When 5.0% of PVAc emulsion was used with both polyester emulsion, the results were slightly increased in the same manner
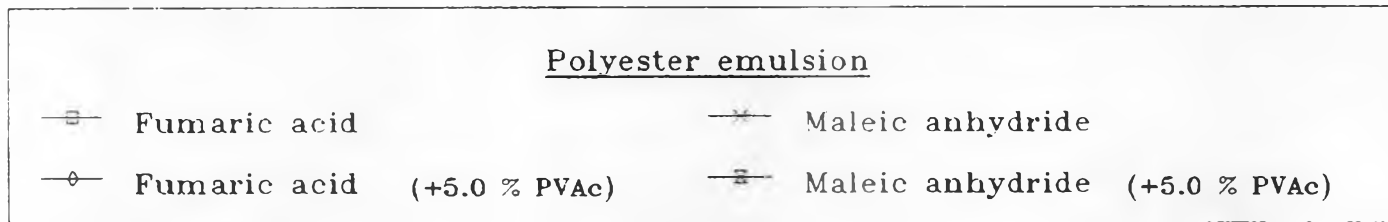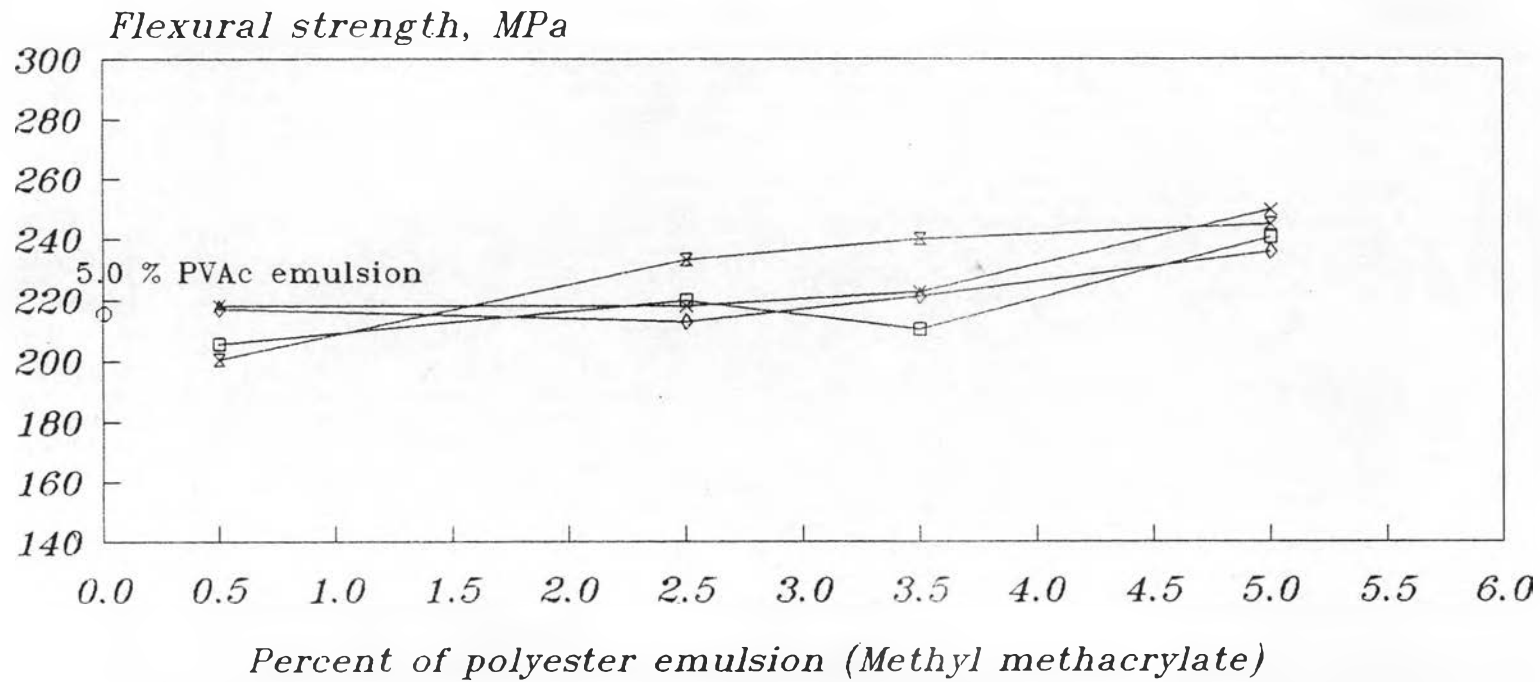
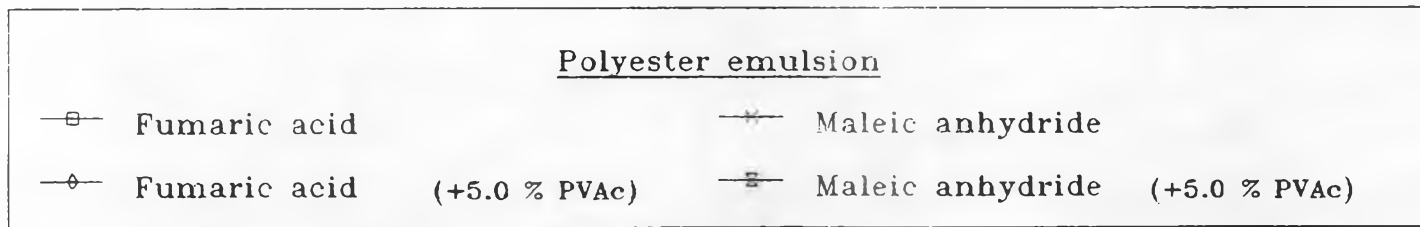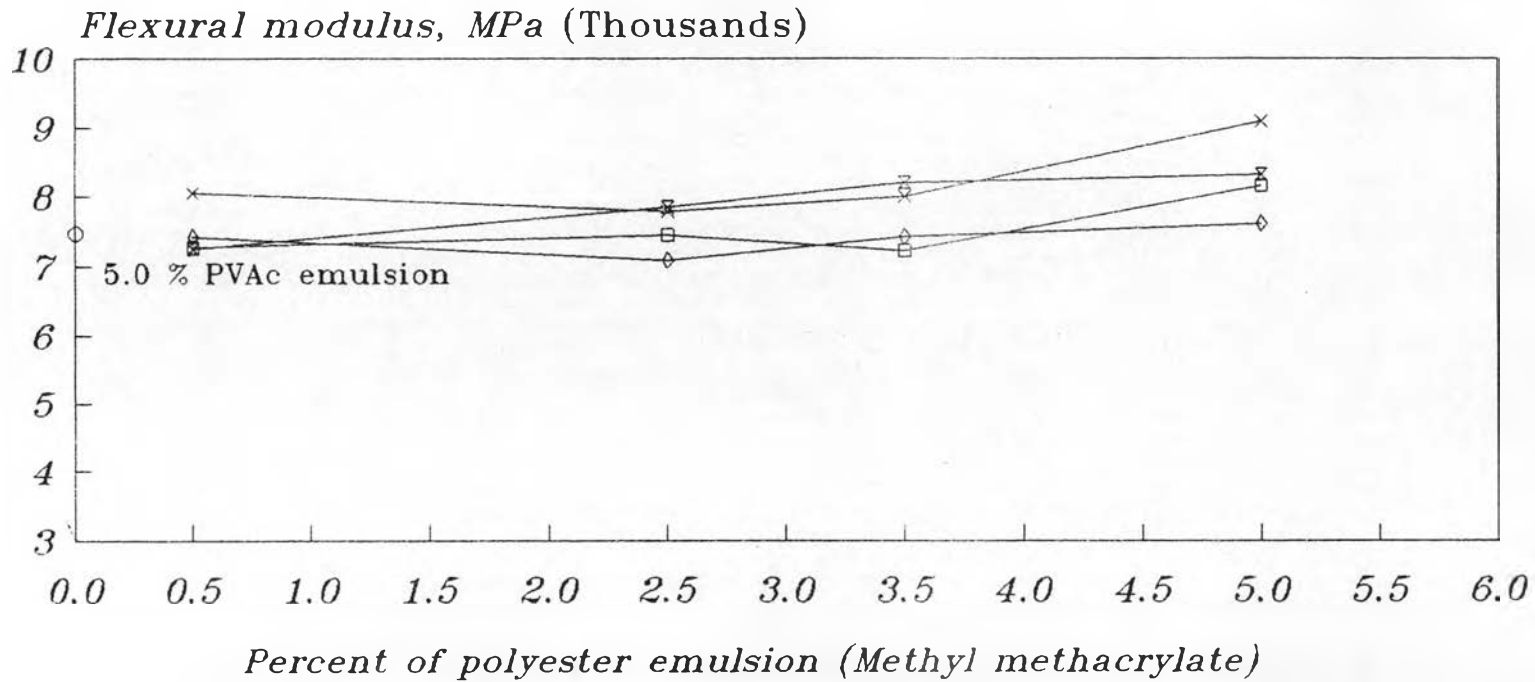Figure 4.27 Flexural strength of the laminates using methyl methacrylate as crosslinking agent

Figure 4.28 Flexural modulus of the laminates using methyl
methacrylate as crosslinking agent

as pure both polyester emulsion. Because of PVAc has $-O\overset{\overset{O}{\|}}{C}CH_3$ group that is a bulky side group which is bigger than the carbonyl group of both polyester emulsions. Thus it will shield the carbonyl group from crosslinked with polyester resin