CHAPTER III

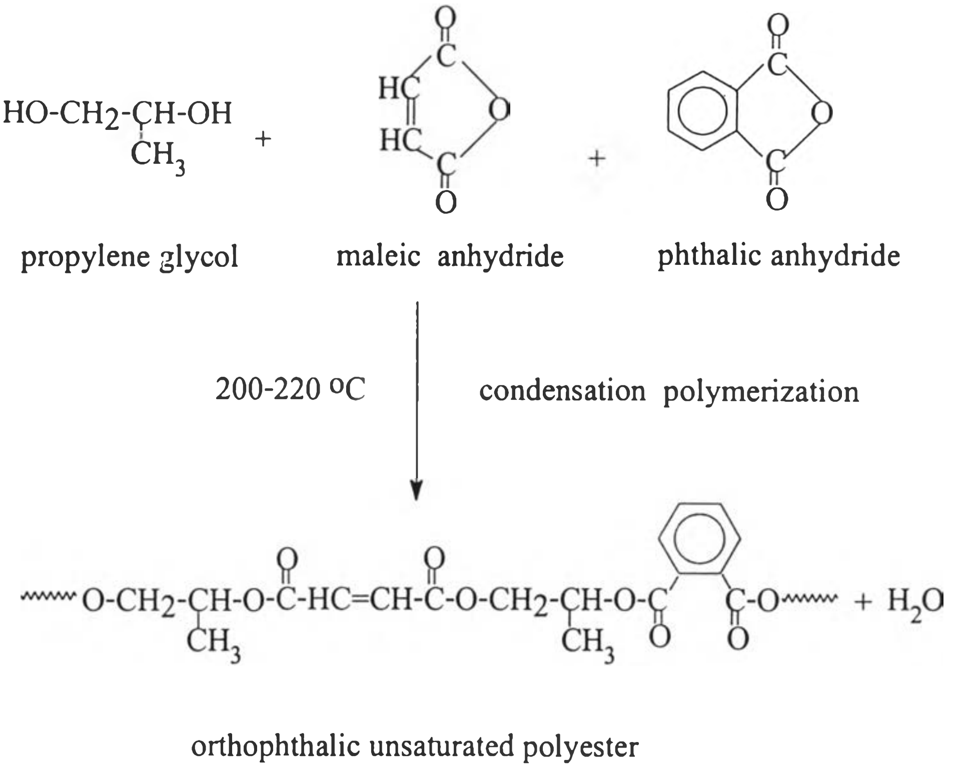
RESULTS AND DISCUSSION

3.1 Preparation of Orthophthalic Unsaturated Polyester (ortho UP) and Isophthalic Unsaturated Polyester (iso UP)

Unsaturated polyesters were prepared by means of condensation polymerization between difunctional acids and alcohols. Generally, acid contributes olefinic unsaturation. In this study, UP with different acid anhydrides or diacid were used. Ortho UP was synthesized from orthophthalic anhydride, maleic anhydride and propylene glycol as shown in Scheme 3.1. Iso UP was synthesized from isophthalic acid, maleic anhydride and propylene glycol as shown in Scheme 3.2.

3.1.1 Reaction Condition

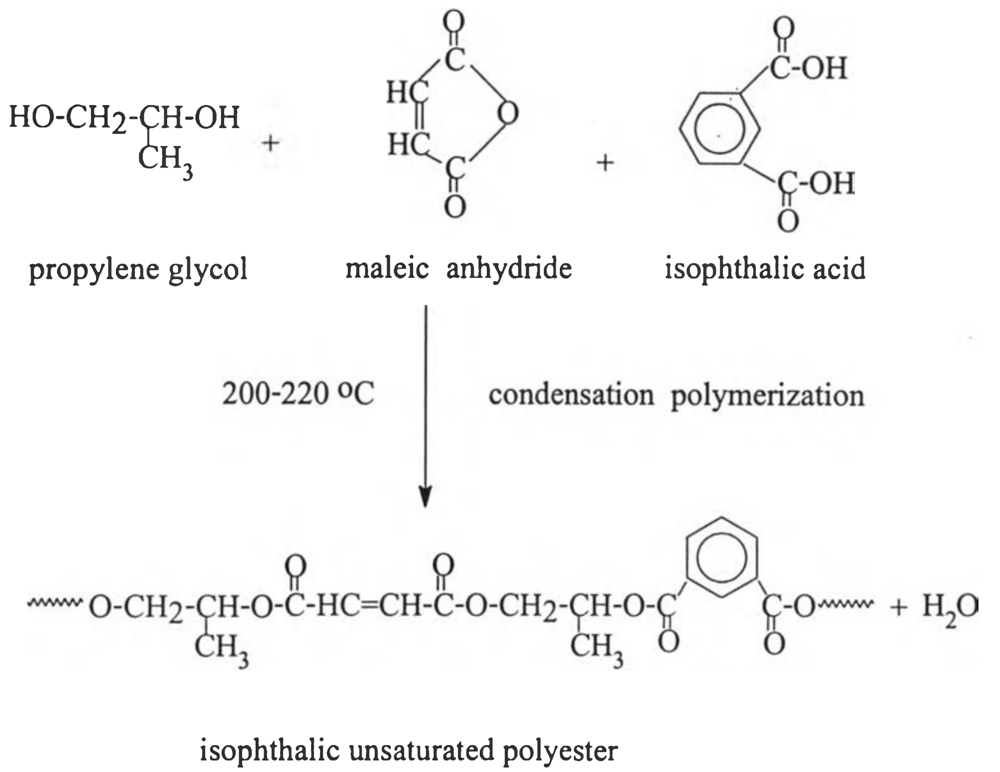
The reaction was carried out under nitrogen atmosphere at the reaction temperature of 200-220°C. The determination of acid number and viscosity (standard Gardner scale), were done every hour throughout the reaction. The reaction was continued until the acid number and acid value had fallen to the end point according to the processdeveloped by Eternal Resin Co., Ltd. The reaction was then cooled until the temperature of polyester was about 150°C.



Scheme 3.1 Preparation of ortho UP

3.1.2 Molecular Weight Determination

The molecular weights of ortho and iso UP and their distributions were determined using GPC with tetrahydrofuran as a solvent. The weight–average molecular weights ($\overline{M}_w$) were obtained in the range of 3000 for the ortho UP and up to 10000 for the iso UP. The molecular weight distributions of ortho and iso UP were 2.0 and 4.0, respectively.



Scheme 3.2 Preparation of iso UP

3.2 Preparation and Characterization of Orthophthalic Unsaturated Polyester Resin (ortho UPR) and Isophthalic Unsaturated Polyester Resin (iso UPR)

The obtained ortho and iso UP were dissolved in a mixture of styrene and MMA to obtain ortho and iso UPR, respectively. Their properties were determined as follows:

3.2.1 Viscosity

The viscosity of the UPR at a given solid in SM and MMA is a direct indication of the degree of polyesterification and molecular weight. The viscosity of ortho and iso UPR were reduced by the addition of MMA. As shown in Figure 3.1, increasing the amount of MMA decreased the viscosity of the UPR. The iso UPR showed greater viscosity than the ortho UPR since it had higher molecular weight.

3.2.2 Non-volatile Content

The non-volatile content of ortho and iso UPR were controlled at 65 wt% of UP as shown in Figure 3.2.

3.2.3 Acid Value

The acid value is the residue of free acid in UPR that is varied by weight ratio of UP. The Acid value of ortho and iso UPR were 23 and 11 mg KOH/g, respectively as shown in Figure 3.3. Both ortho and iso UPR from varied compositions of UP : SM : MMA showed almost the same acid value.

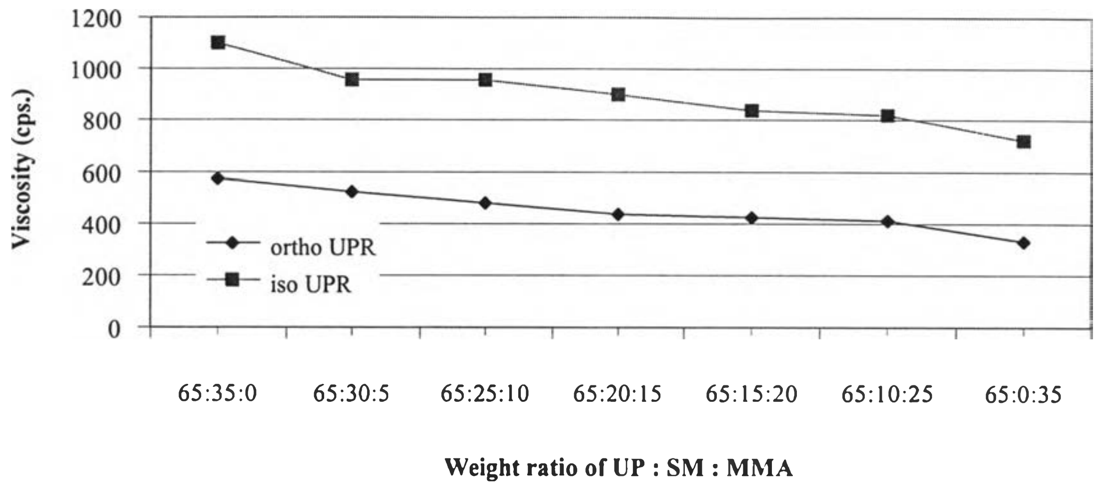


Figure 3.1 Relationship between viscosity of UPR and weight ratio of UP : SM : MMA

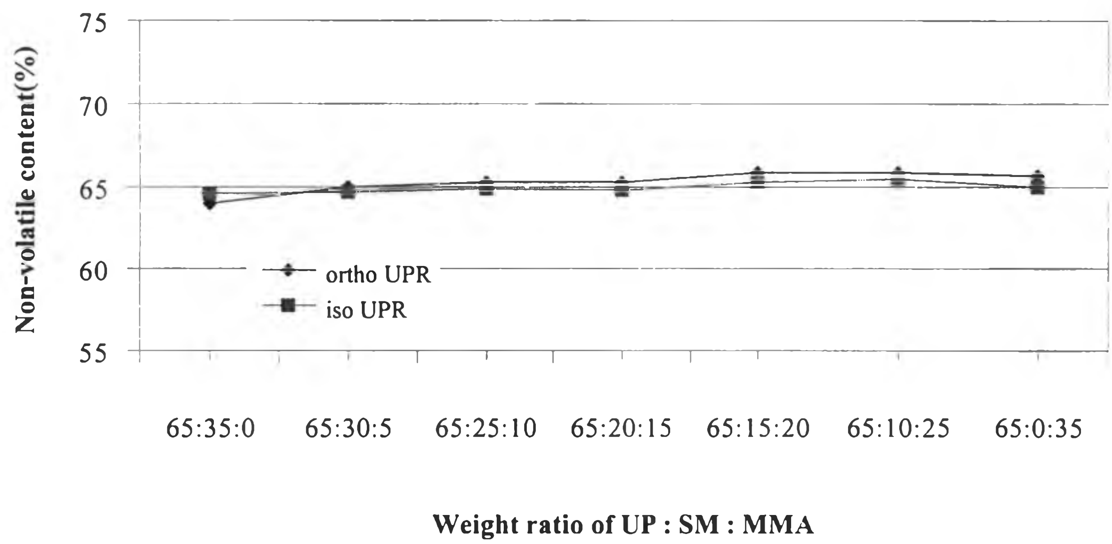


Figure 3.2 Relationship between non-volatile content of UPR and weight ratio of UP : SM : MMA

3.2.4 Gel time and Curing Properties

3.2.4.1 Cup Gel Test

From Figure 3.4, it can be seen that increasing the amount of MMA resulted in increase of the gel time of both Ortho and iso UPR. This is because the reactivity ratio of MMA (0.48) is lower than the reactivity ratio of SM (0.52).(27) The iso UPR showed greater gel time than the ortho UPR.

3.2.4.2 SPI Gel Test

3.2.4.2.1 Gel Time and Cure Time

The gel time of ortho UPR and iso UPR were also measured by SPI gel test (Figure 3.5). When the ratios of UP : SM : MMA was varied, the gel time obtained from SPI test showed the same trend as in the case of cup gel test. As shown in Figure 3.6, increasing the amount of MMA in formulation resulted in the increase in the cure time of UPR. The ortho UPR showed greater gel time and cure time than the iso UPR. The ratio of 65 : 0 : 35 showed the longest gel time and cure time.

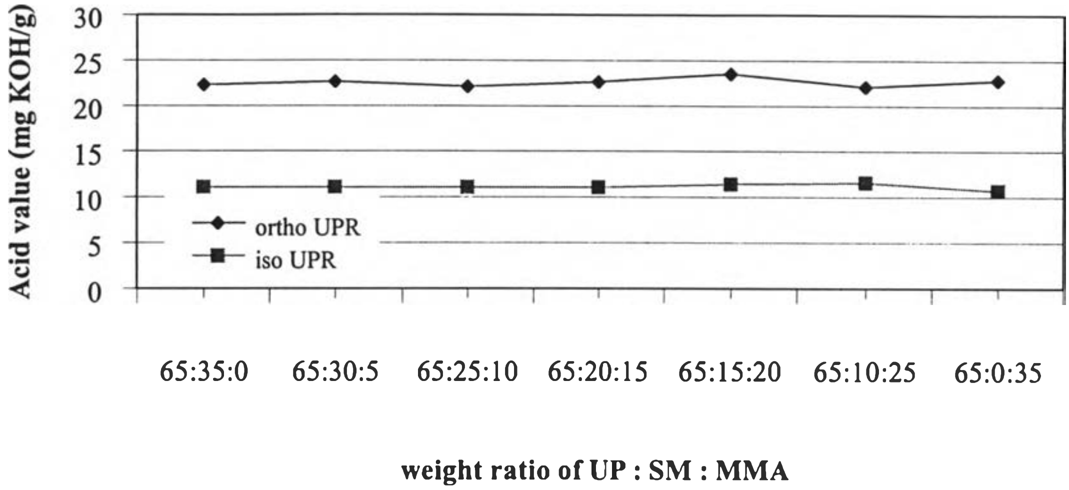


Figure 3.3 Relationship between acid value of UPR and weight ratio of UP : SM : MMA

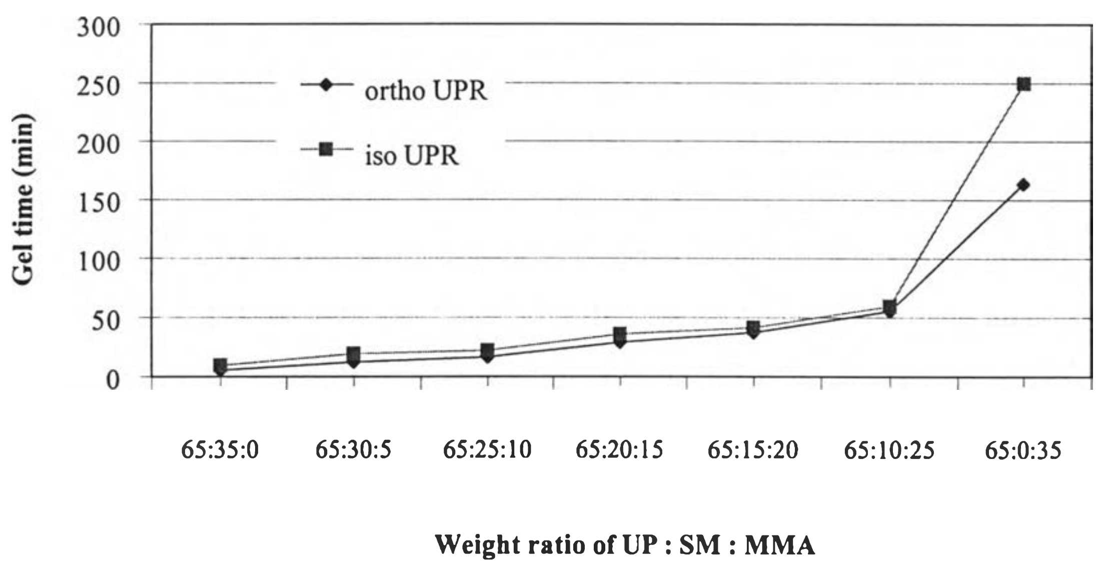


Figure 3.4 Relationship between gel time of UPR at 25°C by measured by cup gel test and weight ratio of UP : SM : MMA

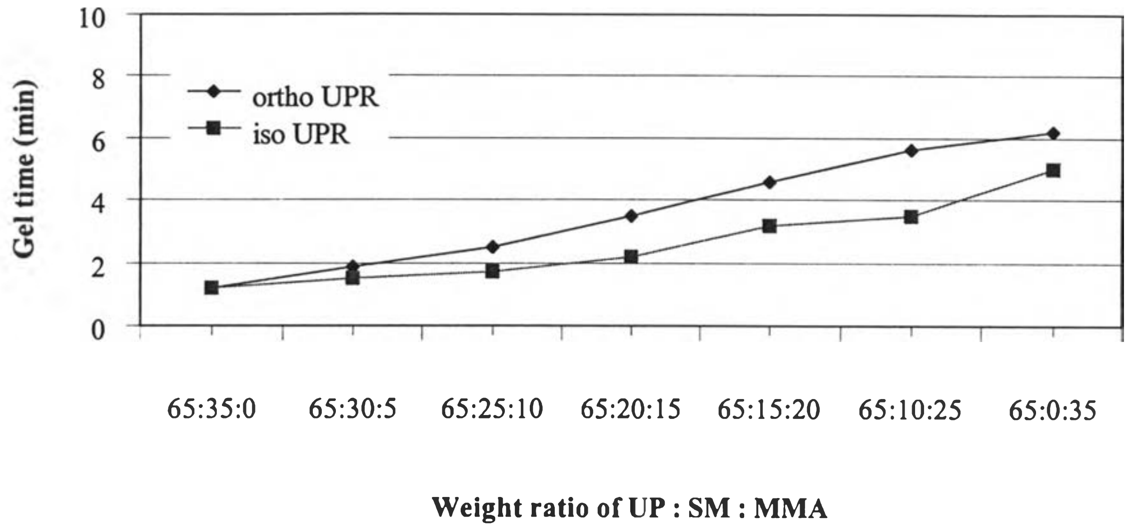


Figure 3.5 Relationship between gel time of UPR at 60°C measured by SPI gel test and weight ratio of UP : SM : MMA

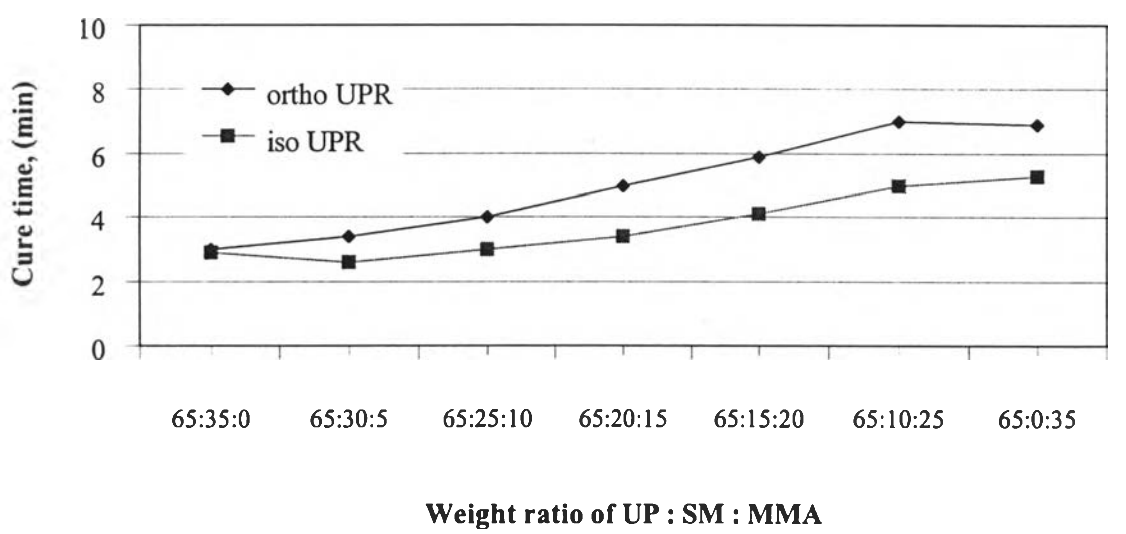


Figure 3.6 Relationship between cure time of UPR at 60°C and weight ratio of UP : SM : MMA

3.2.4.2.2 Exothermic Peak Temperature

The ortho and iso UPR with higher ratios of MMA showed lower exothermic peak temperature due to the lower reactivity of MMA which leaded to a slow cure. Iso UPR showed greater exothermic peak temperature than ortho UPR. Figure 3.7, shows the effect of variation in the UP : SM : MMA ratio on the exothermic peak temperature.

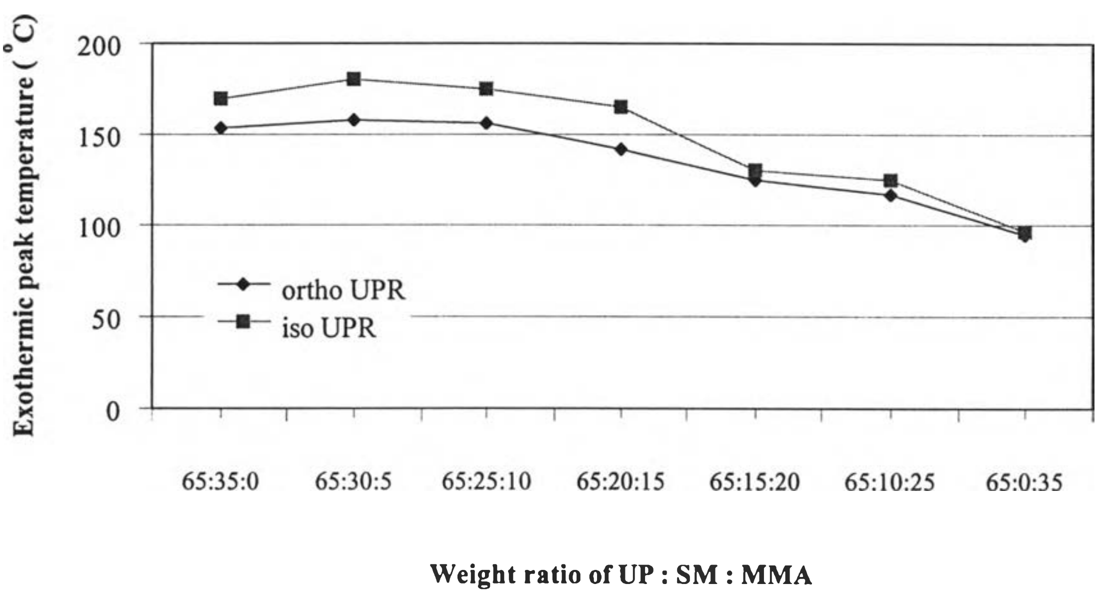


Figure 3.7 Relationship between exothermic peak temperature of UPR at 60°C and weight ratio of UP : SM : MMA

3.3 Mechanical Properties of Orthophthalic Thermoset Polyester (ortho thermoset polyester) and Isophthalic Thermoset Polyester (iso thermoset polyester)

The addition of MMA to an unsaturated polyester resin for weathering improvement affects mechanical and chemical properties of the thermoset polyester. In this study, the tensile strength , flexural strength, heat distortion temperature and hardness were examined.

3.3.1 Tensile Strength

The effects of MMA on tensile properties of the ortho and iso thermoset polyesters were shown in Figures 3.8 and 3.9, respectively. The tensile strength of ortho thermoset polyester from the varied compositions of UP : SM : MMA were in the range of 34-40 N/mm^2. Variation of the MMA amount in the formulation had no effect of tensile value except at the ratio of UP : SM : MMA = 65 : 10 : 25 where the decrease in tensile value was observed. At the ratio of UP : SM : MMA = 65 : 0 : 35, the obtained material was too brittle to measure its tensile strength.

The tensile strength of iso thermoset polyester was expected to be higher than that of ortho thermoset polyester. However, both ortho and iso thermoset polyesters showed almost the same tensile value. This was due to the high viscosity of iso UPR that caused bubble formation during the preparation of thermoset polyester. The highest tensile value was observed at the ratio of iso UP : SM : MMA = 65 : 15 : 20.

The changes in MEKPO amount in the formulation of ortho and iso thermoset polyester had small effect in tensile strength. Therefore, 0.5-2.0% of MEKPO can be used in the industrial application. This is beneficial since large objects require less MEKPO in the formulation.

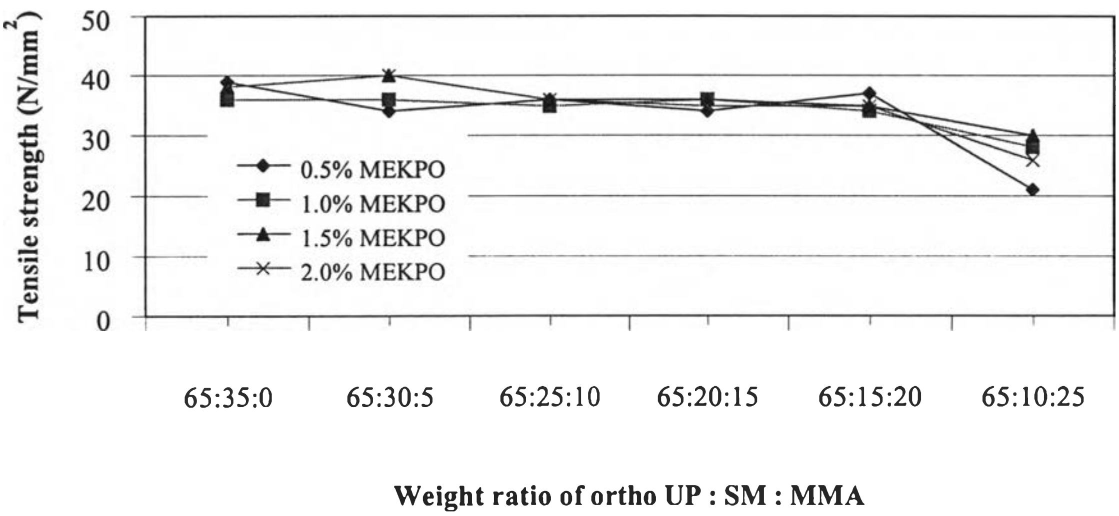


Figure 3.8 Relationship between tensile strength of ortho thermoset polyesters and weight ratio of ortho UP : SM : MMA at different % v/wt of MEKPO

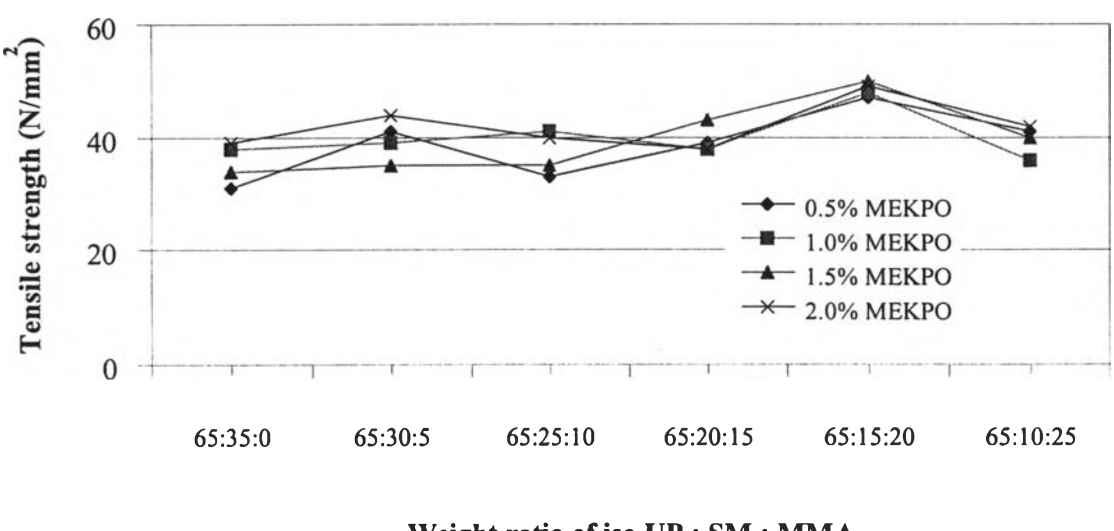


Figure 3.9 Relationship between tensile strength of iso thermoset polyesters and weight ratio of iso UP : SM : MMA at different % v/wt of MEKPO

3.3.2 Flexural Strength

Figures 3.10 and 3.11 present the flexural strength of ortho and iso thermoset polyesters, respectively. The flexural strength of ortho thermoset polyester from the varied compositions of UP : SM : MMA were in range of 65-80 N/mm^2. The changes in UP : SM : MMA ratio or amount of MEKPO in the formulation had small effect in the flexural strength.

The flexural strength of iso thermoset polyester were in the range of 80-105 N/mm^2 and were higher than those of ortho thermoset polyester. Variation of the UP : SM : MMA ratio or MEKPO amount also had small effect in the flexural strength.

3.3.3 Hardness

Rockwell Hardness can be obtained by measuring the resistance to penetration by spherical point. Figures 3.12 and 3.13 show the effect of the variation in UP : SM : MMA ratio and amount of MEKPO on the hardness of ortho and iso thermoset polyesters. Their hardness values were in the range of 95-106. At the ratios of UP : SM : MMA between 65 : 35 : 0 and 65 : 25 : 10, the hardness of ortho and iso thermoset polyesters was in the same range. The iso thermoset polyester showed slightly higher hardness than the ortho thermoset polyester. Changes in the amount of MEKPO had small effect on hardness except at the ratio of UP : SM : MMA = 65 : 20 : 15 where the marked decrease in hardness was observed.

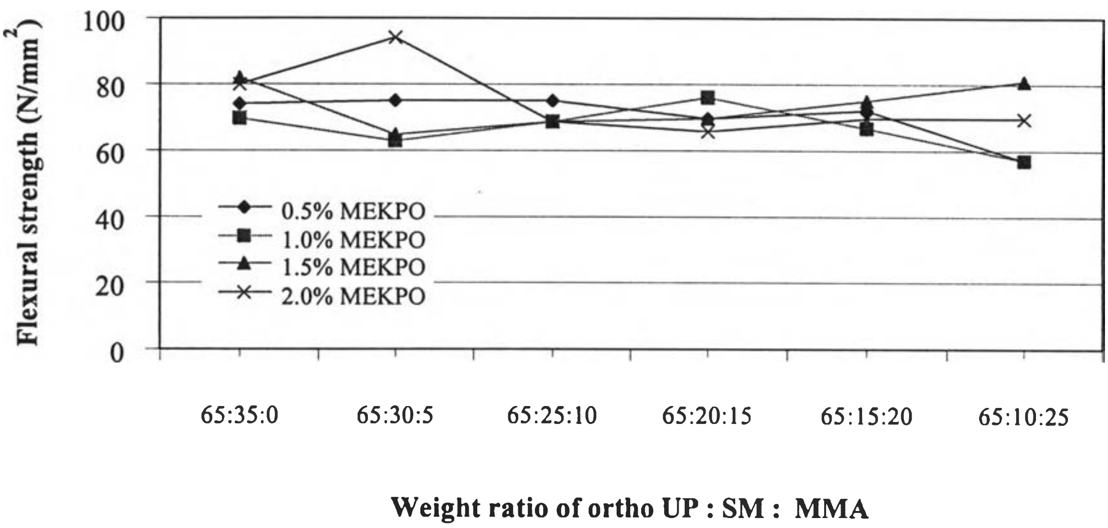


Figure 3.10 Relationship between flexural strength of ortho thermoset polyesters and weight ratio of ortho UP : SM : MMA at different % v/wt of MEKPO

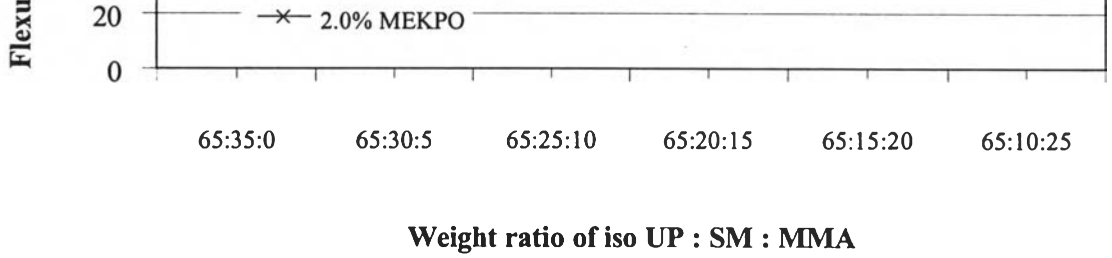


Figure 3.11 Relationship between flexural strength of iso thermoset polyesters and weight ratio of iso UP : SM : MMA at different % v/wt of MEKPO

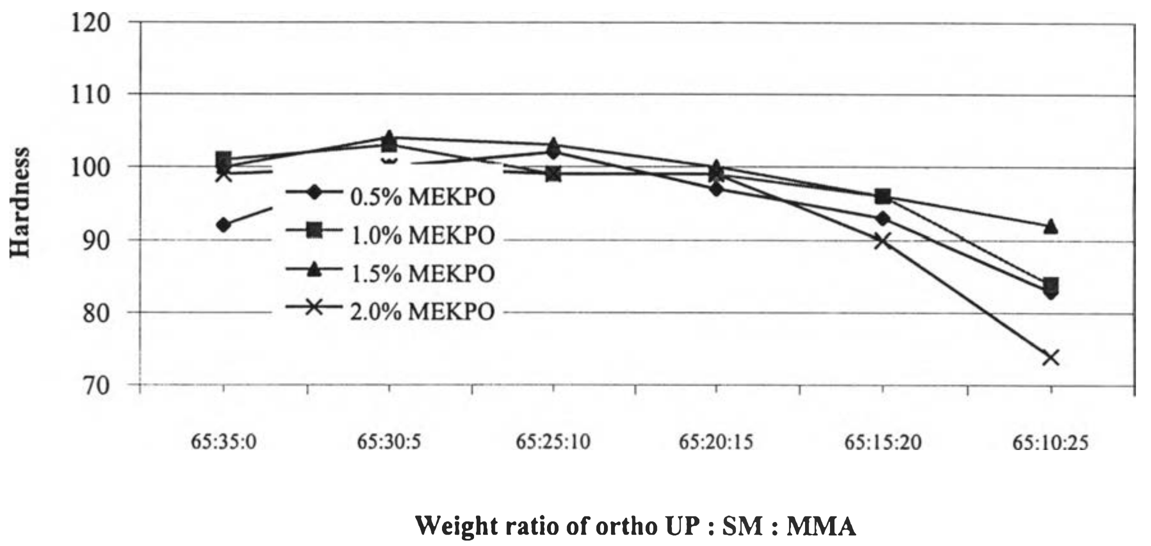


Figure 3.12 Relationship between hardness of ortho thermoset polyesters and weight ratio of ortho UP : SM : MMA at different % v/wt of MEKPO

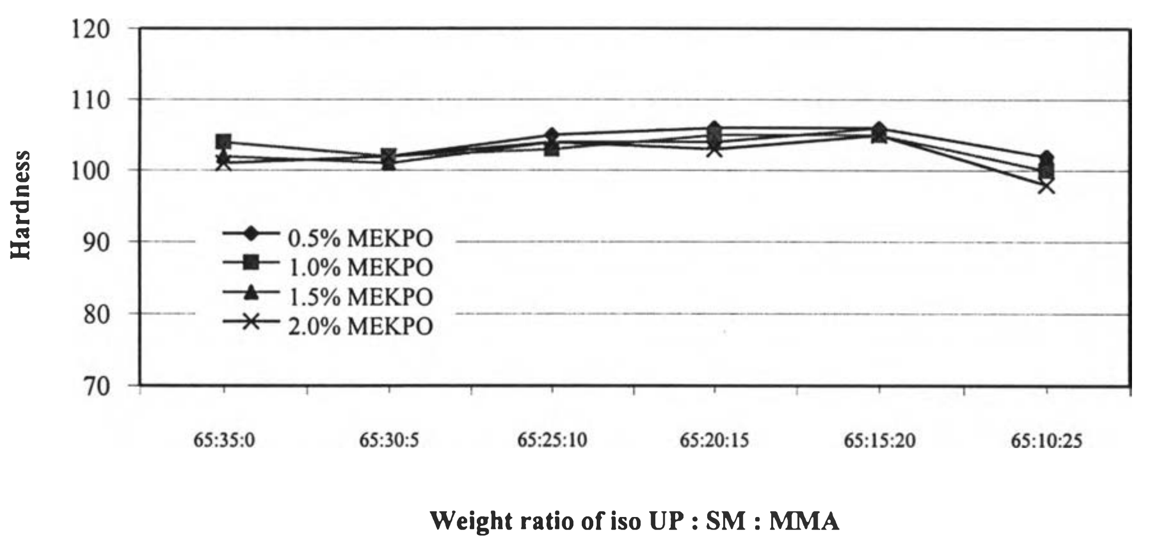


Figure 3.13 Relationship between hardness of iso thermoset polyesters and weight ratio of iso UP : SM : MMA at different % v/wt of MEKPO

3.3.4 Heat Distortion Temperature

Heat distortion temperature is commonly used as an indication of the material strength at elevated temperature. It represents one point on the temperature-deflection curve. The HDT of the ortho and iso UP thermoset polyester were shown in Figures 3.14 and 3.15, respectively. For both ortho and iso thermoset polyester, increase of MMA in the formulation resulted in the decrease of heat distortion temperature. Changes in the amount of MEKPO had no effect on heat distortion temperature. The iso thermoset polyester showed higher heat distortion temperature than the ortho thermoset polyester.

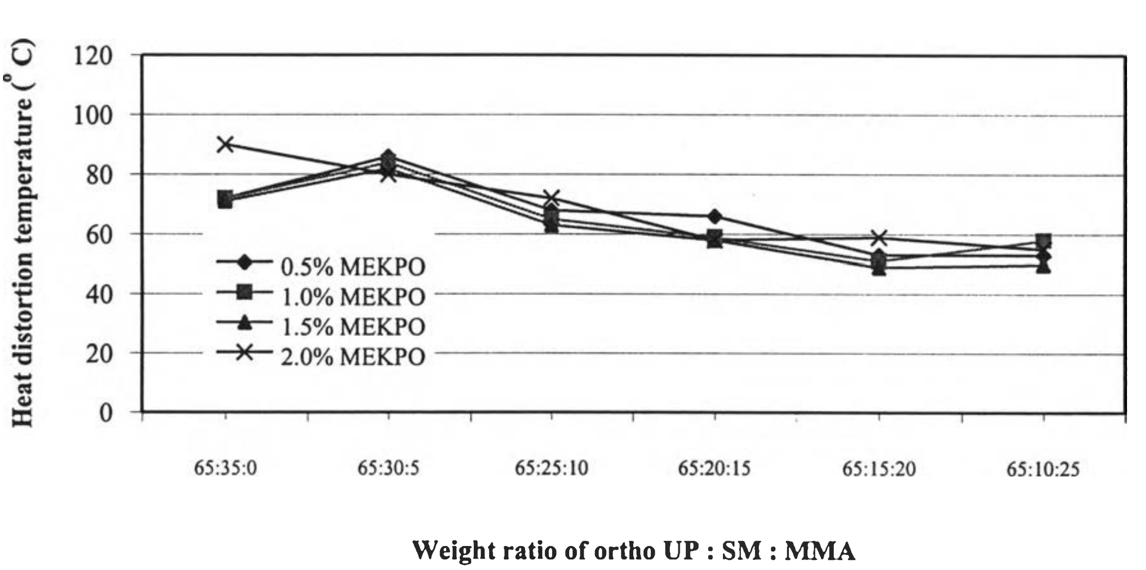


Figure 3.14 Relationship between heat distortion temperature of ortho thermoset polyesters and weight ratio of ortho UP : SM : MMA at different % v/wt of MEKPO

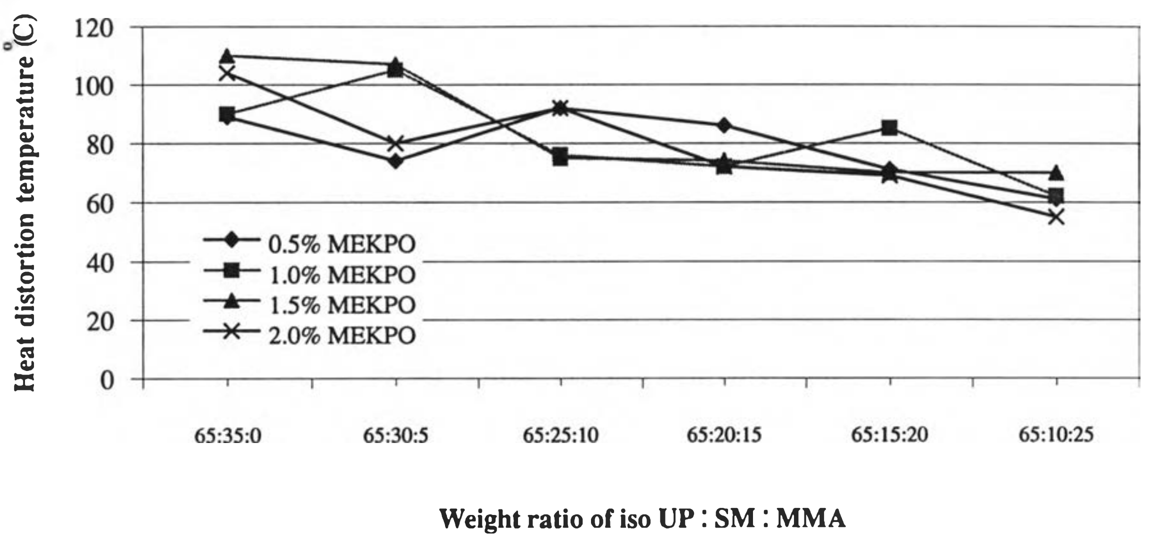


Figure 3.15 Relationship between heat distortion temperature of iso thermoset polyesters and weight ratio of iso UP : SM : MMA at different % v/wt of MEKPO

3.3.5 Weathering Resistance

The results from weathering resistance test by using Q-U-V- accelerator weathering tester are shown in Figures 3.16 and 3.17. By comparing with the reference sample, the thermoset polyester with good weathering resistance should not change in color after the test. If the thermoset polyester does not have good weathering resistance, its color will change to yellow after the test. For both ortho and iso thermoset polyesters, increase in the amount of MMA in the formulation resulted in the improvement on the weathering resistance. Therefore, the ratio of 65 : 10 : 25 showed the best weathering resistance. Changes in amount of MEKPO in the curing process did not effect the weathering resistance. The appearance of iso thermoset polyester is more yellowish than ortho thermoset polyester, however, that its application does not concern the clear application.

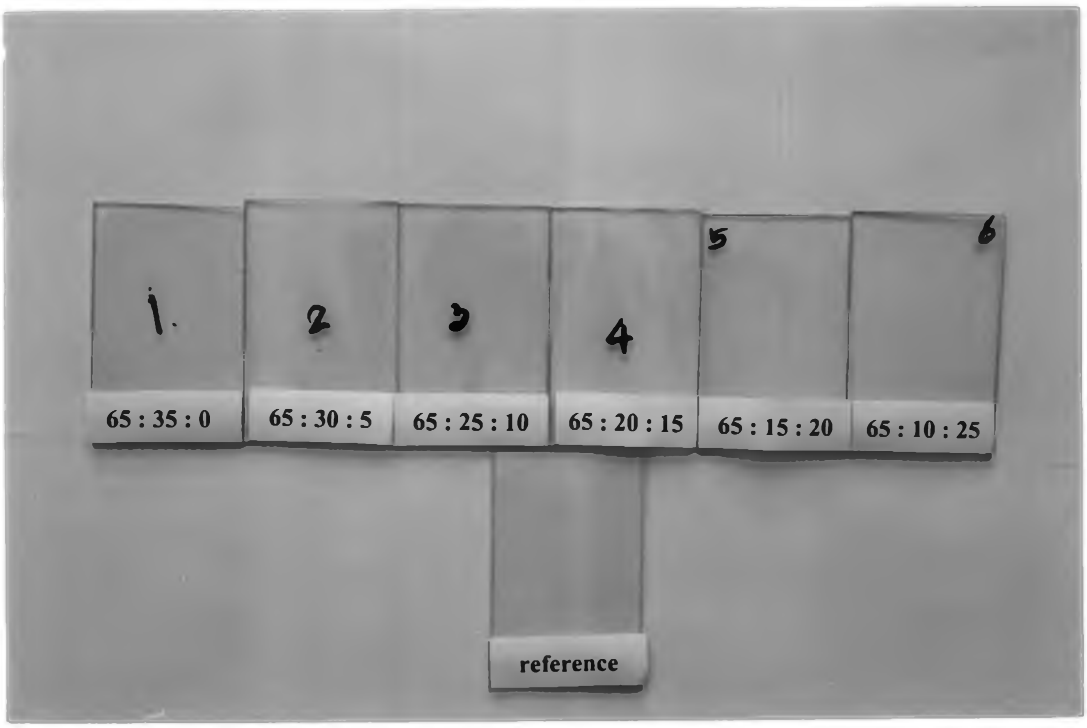


Figure 3.16 Weathering resistance of the ortho thermoset polyesters at different ratios of ortho UP : SM : MMA and 1.0% v/wt of MEKPO was used.

Figure 3.17 Weathering resistance of the iso thermoset polyesters at different ratios of iso UP : SM : MMA and 1.0% v/wt of MEKPO was used.

From the above results, variation in the ratio of UP : SM : MMA had small effect on the tensile strength, flexural strength, hardness and weathering resistance of both ortho and iso thermoset polyesters. The effect resulted from the variation of UP : SM : MMA ratio could be seen in the change in heat distortion temperature. Therefore, the UP : SM : MMA ratio suitable for application was chosen from the formulation that gave the highest heat distortion temperature. The suitable ratio of ortho UP : SM : MMA is 65 : 30 : 5 and that of iso UP : SM : MMA is 65 : 15 : 20. These formulations were chosen for the preparation of fiber reinforced thermoset polyesters.

3.4 Fibre Reinforced Plastic (FRP) of Orthophthalic Unsaturated Polyester Resin (ortho FRP) and Isophthalic Unsaturated Polyester Resin (iso FRP)

In this study, the ortho UPR at the ratios of 65 : 30 : 5, 65 : 10 : 25 and iso UPR at the ratio of 65: 15: 20 were combined with glass fiber. Their tensile strength, flexural strength hardness and heat distortion temperature were examined as shown in Table 4.1. The tensile strength of ortho and iso FRP were greater than those of thermoset polyesters. Although the 65 : 10 : 25 of ortho thermoset polyester showed low tensile strength, its FRP showed high tensile strength. In comparison to the ortho thermoset polyester at the ratio of 65 : 30 : 5 which showed good tensile strength, the FRP obtained from this ratio showed almost the same tensile value as the FRP obtained from the ratio of 65 : 10 : 25. The same trend was also observed in flexural strength. Regarding the hardness value, the FRP showed almost the same value as in the thermoset polyestter. The heat distortion temperature of FRP was also higher than those of the thermoset polyesters. The ortho FRP of the ratio 65 : 30 : 5 showed much higher heat distortion temperature than the ortho thermoset polyester of the same ratio. The iso FRP obtained from the ratio 65 : 15 : 20 showed the same trend as in the case of ortho FRP at the ratio of 65 : 30 : 5.

In summary, preparation of FRP both from ortho and iso UPR resulted in better physical and mechanical properties. Iso FRP shows higher tensile strength and heat distortion temperature than ortho FRP.

Table 4.1 Physical and mechanical properties of FRP
(sample size for tensile strength testing = 300 mm x 25 mm x 3 mm)

Weight ratio of	Tensile strength (N/mm^2)		Flexural strength (N/mm^2)		Hardness		heat distortion temperature (°C)	
UP : SM : MMA	Thermoset polyester	FRP	Thermoset polyester	FRP	Thermoset polyester	FRP	Thermoset polyester	FRP
Ortho UPR 65 : 30 : 5	40	78	95	162	100	102	64	121
Ortho UPR 65 : 10 : 25	26	83	70	165	74	89	59	68
Iso UPR 65 : 15 : 20	49	86	92	167	105	103	69	148