CHAPTER V

RESULTS AND DISCUSSION

5.1 DEPOLYMERIZATION OF PET

5.1.1 Product from depolymerization

PET flakes were depolymerized by glycolysis in an excess EG and PG mixture with zinc acetate as catalyst at 190-200 °C , 1 atm . It was found that PET flakes dissolved after about half an hour. At the end of reaction PET flakes were not remained in the reactor.Glycolyzed product before removal of free glycol was blue paste. The more the excess EG and PG, the more watery glycolyzed product was. Glycolyzed product before removal of free glycol was showed in Figure 5-1.

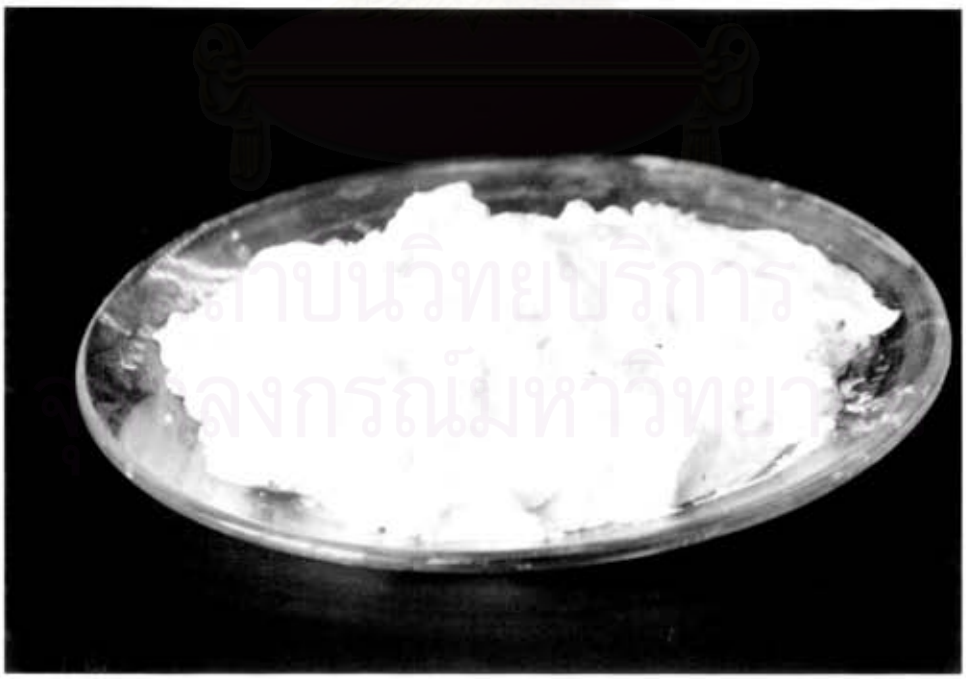

Figure 5-1 Glycolyzed product before removal of free glycol

Then glycolyzed products were precipitated by distilled water and filtered to remove free glycol. Product obtained from filtration was called glycolyzed product after removal of free glycol, Characteristic of glycolyzed product after removal of free glycol was white powder and it was shown in Figure 5-2.

Figure 5-2 Glycolyzed product after removal of free glycol

Glycolyzed products before and after removal of free glycol were analyzed for hydroxyl value , %free glycol and number average molecular weight.

5.1.2 Effect of depolymerization time

In this part, effect of depolymerization time on depolymerization of PET were studied by analyzing hydroxyl value, % free glycol and number average molecular weight. Depolymerization times were varied, namely, 1, 2, 4, 6 and 8 hrs with a fixed molar ratio (EG+PG)/PET at 1, 2, 3 and 4.

The results of hydroxyl value of glycolyzed product before and after removal of free glycol, % free glycol and number average molecular weight were summarized in Table 5-2, Figure 5-3 and Figure 5-4. illustrating effect of depolymerization time on hydroxyl value of glycolyzed product before and after removal of free glycol. Effect of depolymerization time on % free glycol and number average molecular weight were showed in Figure 5-5 and Figure 5-6, respectively.

Table 5-1 Hydroxyl value , % free glycol and number average molecular weight of glycolyzed product at different depolymerization time at a fixed molar ratio of (EG+PG)/PET 1, 2, 3 and 4

Molar ratio of (EG+PG)/ PET	Depolymerization time (hrs)	Run	Hydroxyl value (mgKOH/g)		% Free glycol (%w/w)	Number average molecular weight
			Before extracted	After extracted		
1	1	gly1,1	612.73	223.14	38.12	502.82
	2	gly2,1	647.96	238.71	36.24	470.03
	4	gly4,1	719.09	276.39	31.03	405.95
	6	gly6,1	731.94	292.55	28.55	383.52
	8	gly8,1	736.99	307.10	28.71	365.35
2	1	gly1,2	742.65	285.66	50.99	392.77
	2	gly2,2	781.05	333.48	50.08	336.45
	4	gly4,2	786.13	345.71	49.37	324.55
	6	gly6,2	809.72	355.35	49.75	315.74
	8	gly8,2	804.58	361.18	44.13	310.65
3	1	gly1,3	817.06	341.27	55.75	328.29
	2	gly2,3	824.75	357.95	54.57	313.45
	4	gly4,3	830.70	382.05	51.59	293.68
	6	gly6,3	842.00	406.62	50.10	276.20
	8	gly8,3	869.52	419.61	50.84	267.39
4	1	gly1,4	801.97	359.96	63.35	311.70
	2	gly2,4	841.67	393.28	63.16	285.29
	4	gly4,4	843.38	398.96	57.91	282.23
	6	gly6,4	851.65	420.33	55.71	266.93
	8	gly8,4	886.41	440.34	54.65	254.80

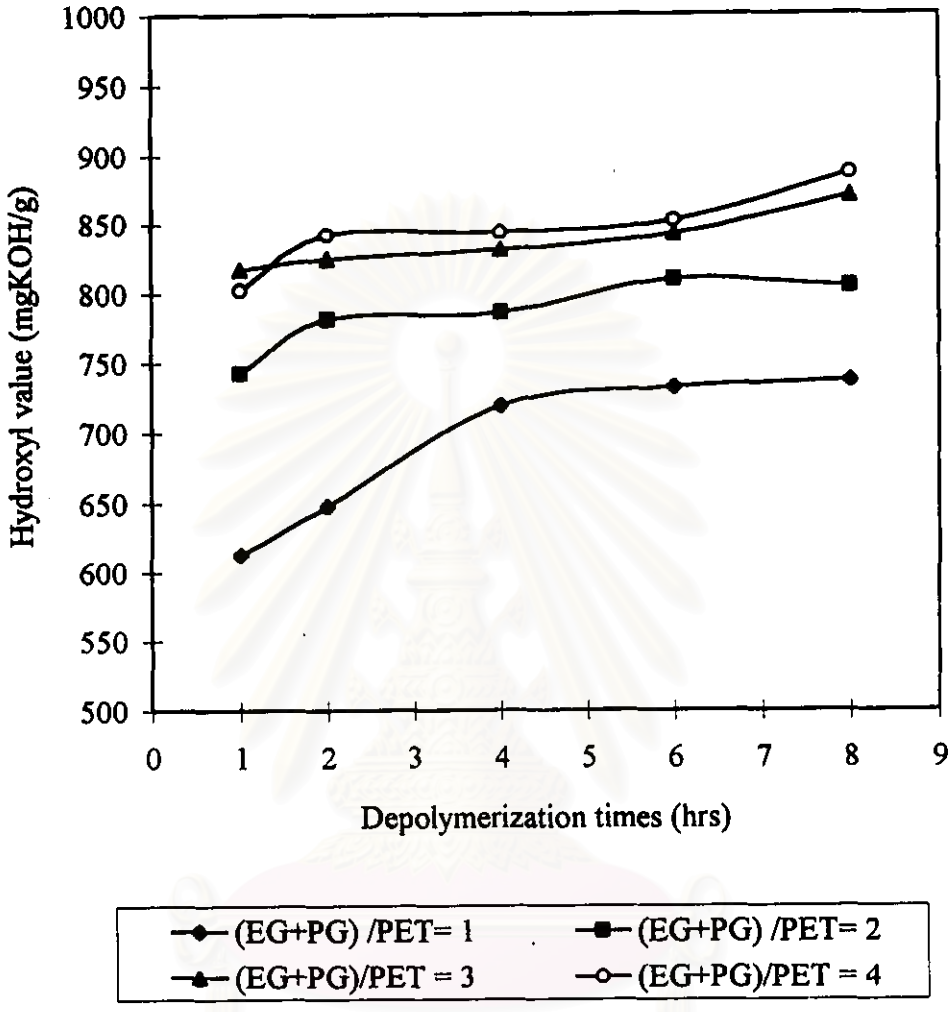

Figure 5-3 Effect of depolymerization time on hydroxyl value of glycolyzed product before removal of free glycol with a fixed molar ratio of (EG+PG)/PET 1, 2, 3 and 4

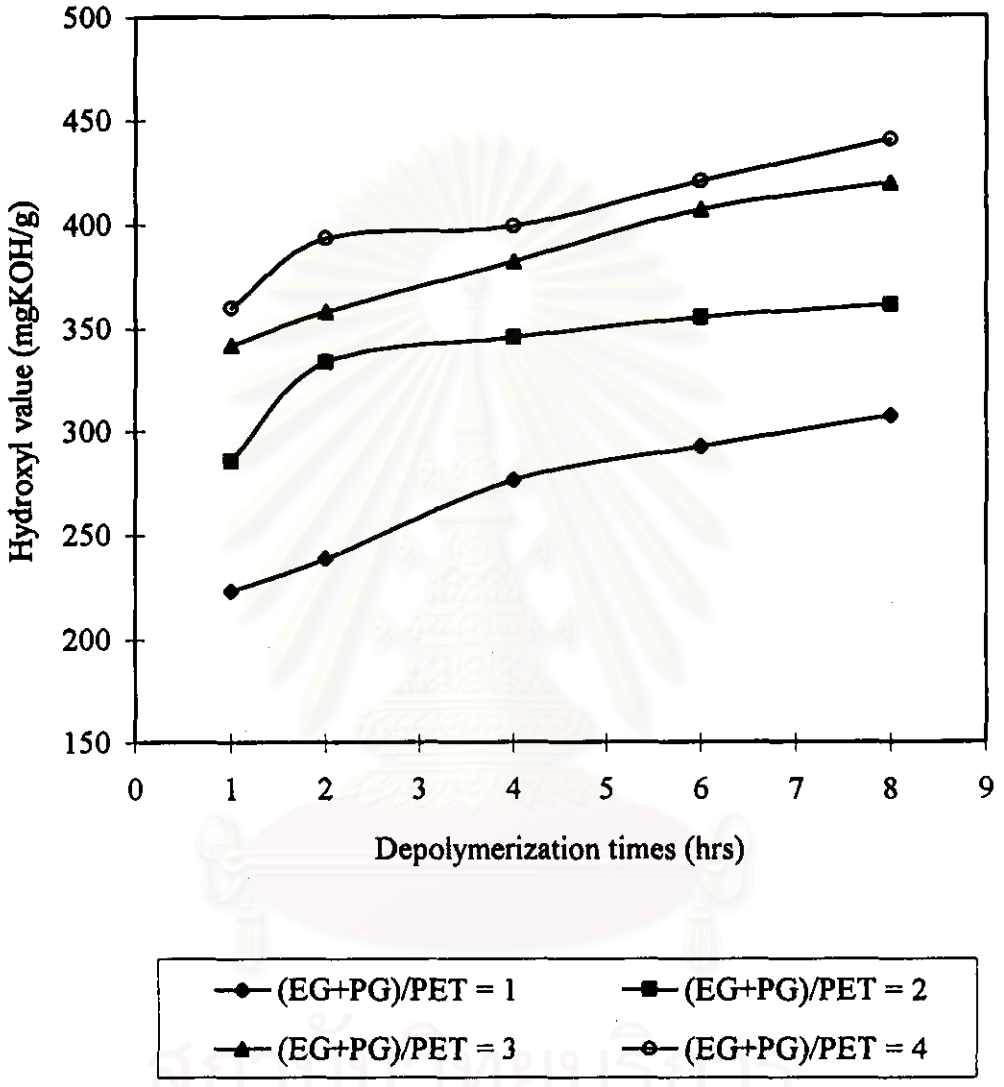

Figure 5-4 Effect of depolymerization times on hydroxyl value of glycolyzed product after removal of free glycol with a fixed molar ratio of (EG+PG)/PET 1, 2, 3 and 4

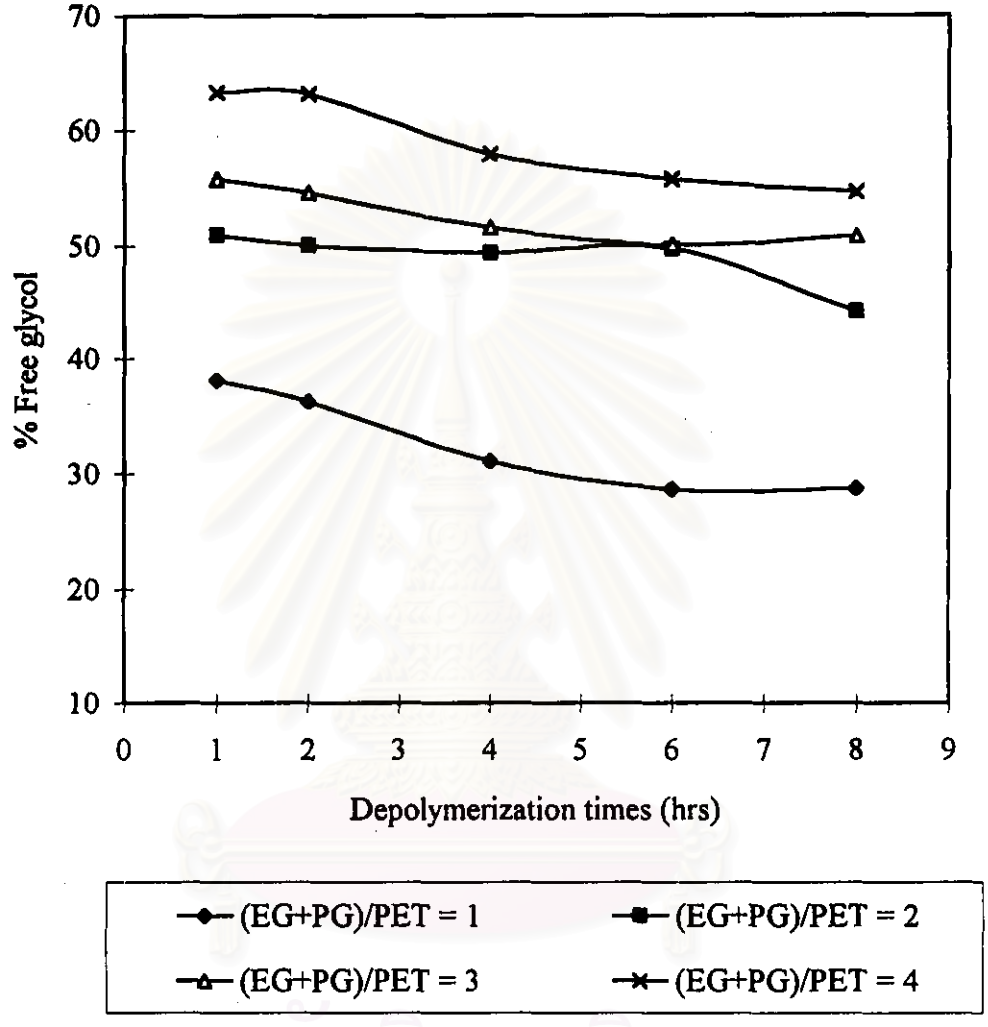

Figure 5-5 Effect of depolymerization times on percent free glycol of glycolyzed product with a fixed molar ratio of (EG+PG)/PET of 1, 2, 3 and 4

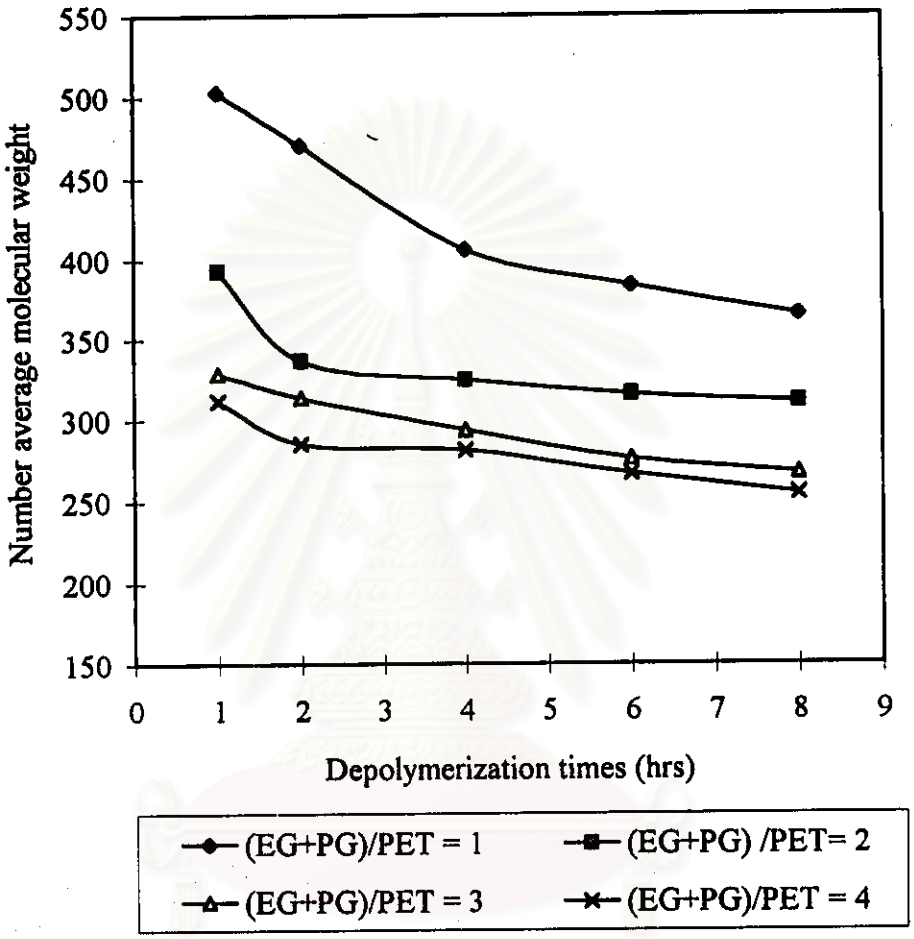

Figure 5-6 Effect of depolymerization times on number average molecular weight of glycolyzed product with a fixed molar ratio of (EG+PG)/PET of 1, 2, 3 and 4

From Figure 5-3 and Figure 5-4 it was found that at constant molar ratio of (EG+PG)/PET when depolymerization time increased , hydroxyl value of glycolyzed product before and after removal of free glycol increased in the same manner.

From Figure 5-7 , we can determined depolymerization rate from slope of curve. Table 5-2 and Figure 5-8 showed depolymerization rate at different depolymerization time.

Table 5-2 Depolymerization rate of glycolyzed product at various depolymerization times

Depolymerization time (hrs)	Depolymerization rate of (EG+PG)/PET molar ratio (Hydroxyl value/ hr)			
	1	2	3	4
0	460.00	767.00	1045.00	1343.00
0.5	166.70	183.33	183.91	204.35
1	79.41	71.90	77.32	85.69
1.5	48.28	42.82	49.04	46.14
2	18.87	24.85	27.25	17.52
3	8.17	9.02	8.51	6.01
4	3.52	2.84	2.69	3.60
6	3.52	2.84	2.69	3.00

From Figure 5-8 decreasing of depolymerization rate was relatively rapid in the first two hourss. About 2 hrs of depolymerization , EG and PG could attack PET chain and depolymerized it into short chain and long chain oligomer. Long chain oligomer was cut off to short chain by EG and PG in next step. In this later step,depolymerization rate was slow because most of the chains were depolymerized to short chains in the early period(< 2hrs).

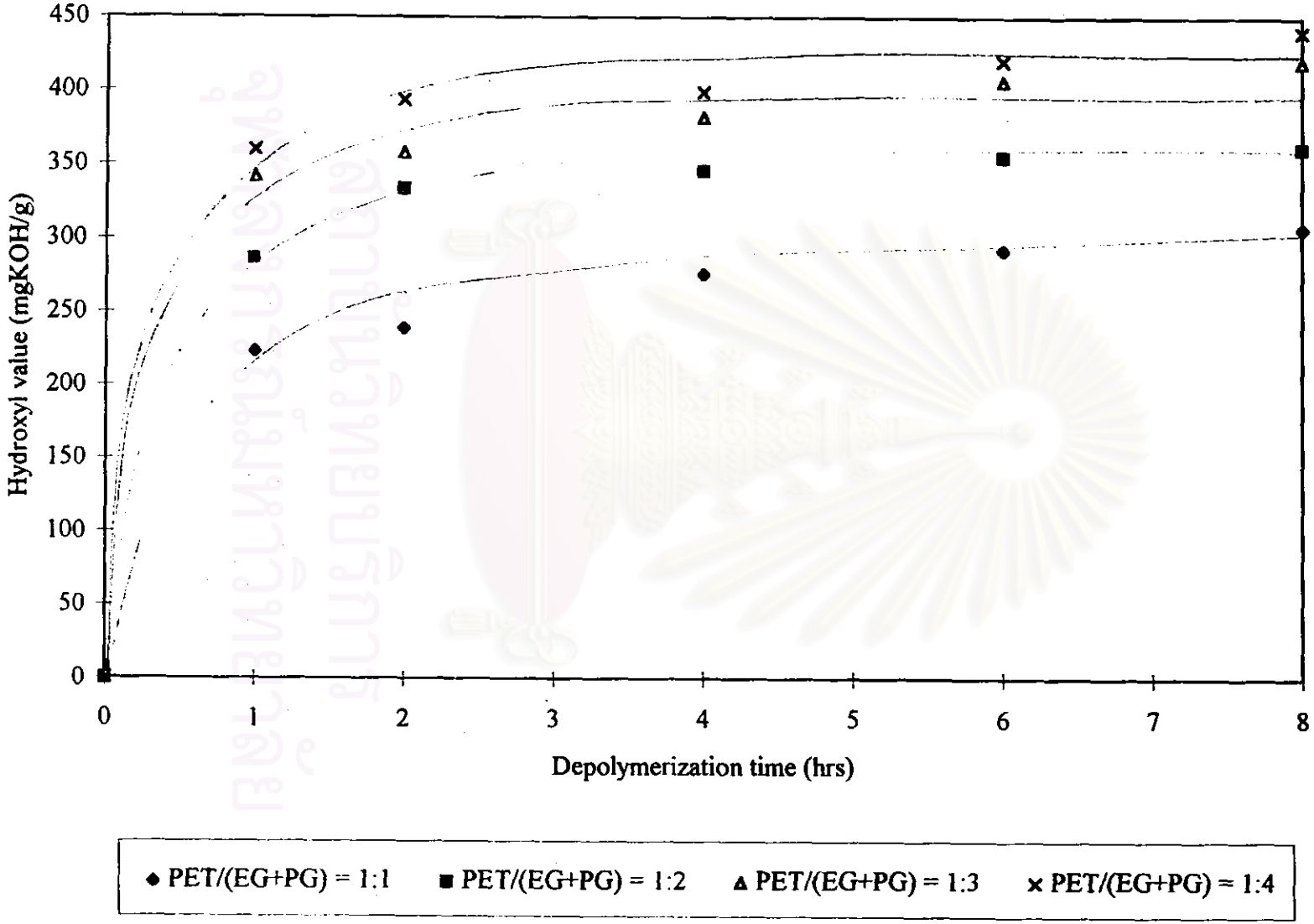

Figure 5-7 Hydroxyl value vs. depolymerization time for determine depolymerization rate

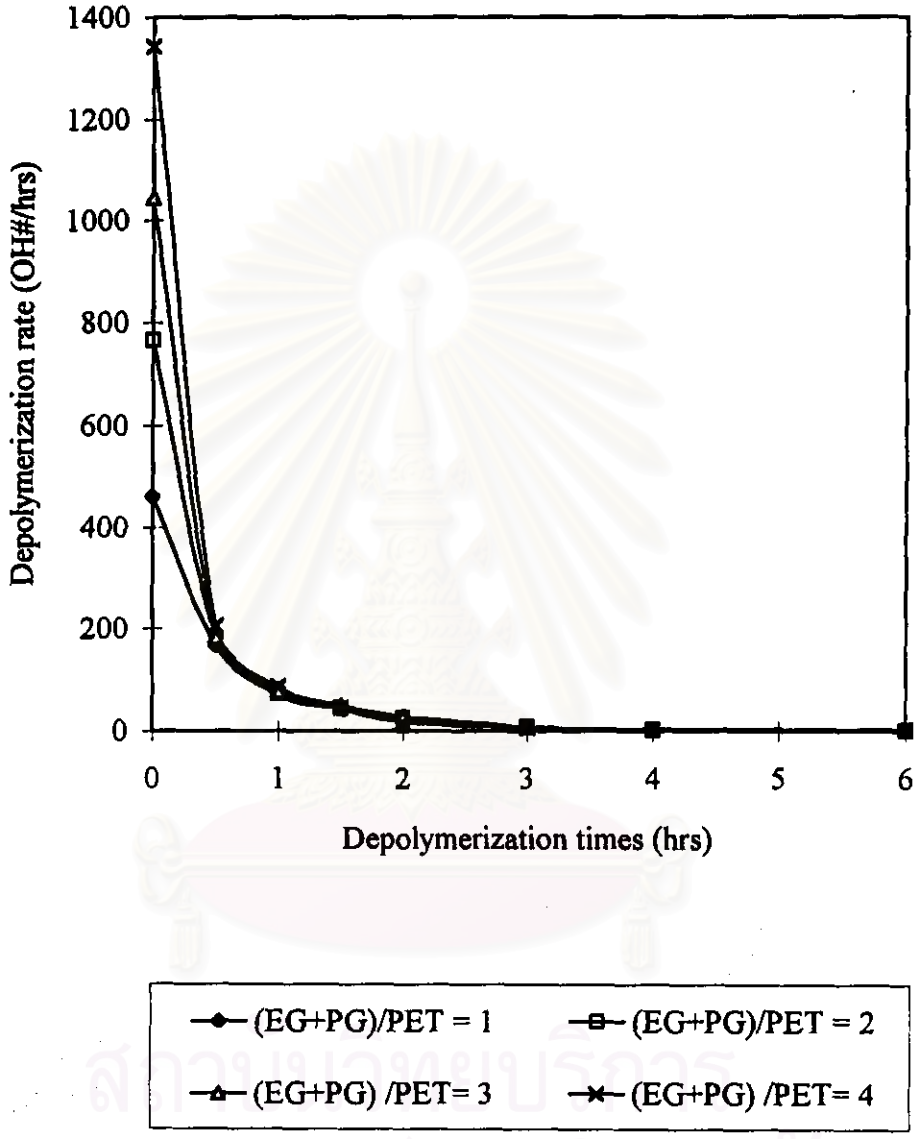

Figure 5-8 Depolymerization rate of glycolyzed product at various depolymerization times by fixed molar ratio of (EG+PG)/PET at 1, 2, 3 and 4

From Figure 5-4, hydroxyl value of glycolyzed product after removal of free glycol remained in the range of 223.14 to 440.34 mgKOH/g for the four molar ratio of (EG+PG)/PET. Baliga and Wong [2] calculated hydroxyl value of BHET and dimer to be 441.5 and 251.3 mgKOH/g, respectively. Thus the range of hydroxyl value of glycolyzed product after removal of free glycol fall between these two values, implying that the glycolyzed products mostly consist of a mixture of BHET and dimer (small amout of oligomer (n>2) may found in glycolyzed product that used less molar ratio of (EG+PG)/PET)).

After 2 hrs of depolymerization time, in Figure 5-8, it was found that depolymerization rate decrease slowly; then equilibrium between BHET , dimer ,EG and PG occurred . Based on these inferences, the following model, consisting of an equilibrium reaction between BHET, dimer, EG, and PG, was proposed for glycolysis of PET [2]:

$$n_{PET}PET + n_{(EG+PG)}(EG+PG) \longrightarrow n_B BHET + n_D DIMER \quad (5\text{-}1)$$

$$2BHET \underset{}{\overset{K}{\rightleftharpoons}} DIMER + (EG+PG) \quad (5\text{-}2)$$

Where n is the number of moles, subscripts B, D, EG and PG stands for BHET, dimer, ethylene glycol and propylene glycol, respectively. The equilibrium constant K is defined as,

$$K = \frac{[D][EG+PG]}{[B]^2} \quad (5\text{-}3)$$

Where [.] is molar concentration. Then, from simple mole balance, it can be shown that

$$a = \frac{[D]}{[B]} = \frac{M_B}{M_D}\frac{H_B - H_I}{H_I - H_D} \quad (5\text{-}4)$$

$$n_B = \frac{1}{1+2a} n_{PET} \quad (5\text{-}5)$$

$$n_D = \frac{a}{1+2a} n_{PET} \quad (5\text{-}6)$$

where

n_{PET} = number of moles of PET repeating units

H_I = measured hydroxyl value of glycolyzed products when reaction reaches equilibrium

M = molecular weight (BHET, 254 ; dimer, 446)

H_B, H_D = theoretical hydroxyl values of BHET(441.5), dimer(251.3)

At constant molar ratio of (EG+PG)/PET and various depolymerization times, percent by mole of BHET and dimer in glycolyzed product at equilibrium can be calculated by using equation (5-3) to (5-6). The results of this calculation was shown in Table 5-3. Figure 5-9 and Figure 5-10 showed effect of depolymerization times on mole precent of BHET and dimer, respectively.

Table 5-3 Mole percent of BHET and dimer in glycolyzed product

Molar ratio of PET/(EG+PG)	Depolym. time (hrs)	Run	H_1 (mgKOH/g)	n_{PET} (mol)	n_B (mol)	n_D (mol)	Mole percent of	
							BHET	DIMER
1:1	1	gly1,1	223.14	0.40	-	-	-	-
	2	gly2,1	238.71	0.40	-	-	-	-
	4	gly4,1	276.39	0.40	0.0471	0.1764	21.07	78.93
	6	gly6,1	292.55	0.40	0.0782	0.1609	32.70	67.30
	8	gly8,1	307.10	0.40	0.1068	0.1466	42.15	57.85
1:2	1	gly1,2	285.66	0.40	0.0649	0.1675	27.92	72.08
	2	gly2,2	333.48	0.40	0.1602	0.1199	57.19	42.81
	4	gly4,2	345.71	0.40	0.1855	0.1072	63.38	36.62
	6	gly6,2	355.35	0.40	0.2058	0.0971	67.94	32.06
	8	gly8,2	361.18	0.40	0.2183	0.0908	70.62	29.28
1:3	1	gly1,3	341.27	0.33	0.1455	0.0922	61.21	38.79
	2	gly2,3	357.95	0.33	0.1744	0.0778	69.15	30.85
	4	gly4,3	382.05	0.33	0.2174	0.0563	79.43	20.57
	6	gly6,3	406.62	0.33	0.2627	0.0336	88.64	11.34
	8	gly8,3	419.61	0.33	0.2874	0.0213	93.10	6.90
1:4	1	gly1,4	359.96	0.25	0.1348	0.0576	70.06	29.94
	2	gly2,4	393.28	0.25	0.1804	0.0348	83.83	16.17
	4	gly4,4	398.96	0.25	0.1882	0.0309	85.90	14.10
	6	gly6,4	420.33	0.25	0.2189	0.0155	93.39	6.61
	8	gly8,4	440.34	0.25	0.2483	0.0009	99.64	0.36

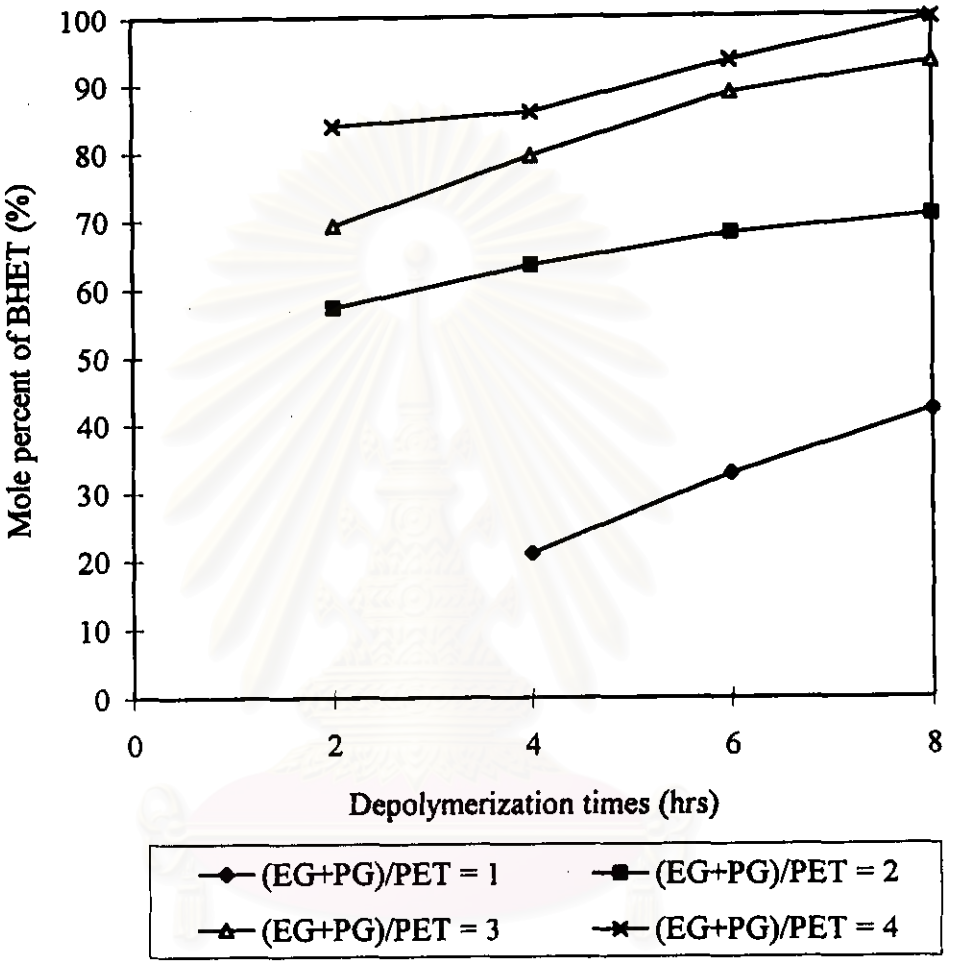

Figure 5-9 Effect of depolymerization times on mole percent of BHET in glycolyzed product with a fixed molar ratio of (EG+PG)/PET 1, 2, 3 and 4

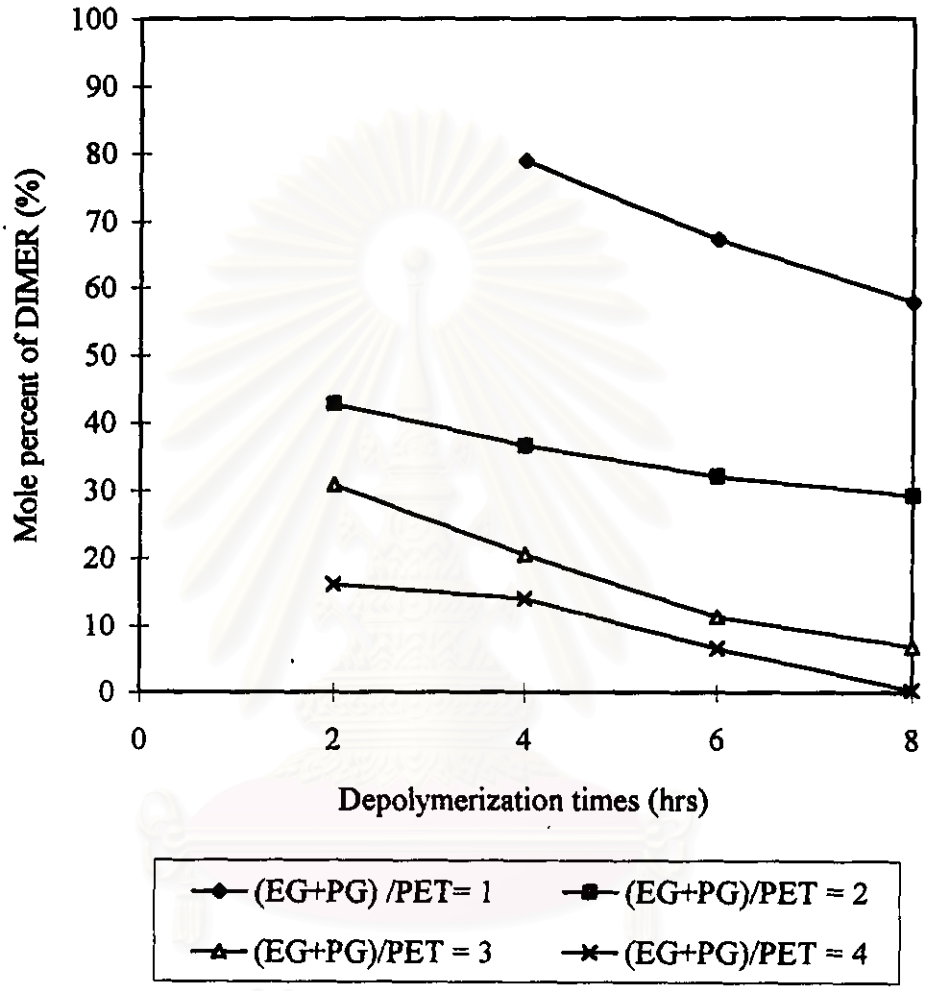

Figure 5-10 Effect of depolymerization times on mole percent of DIMER in glycolyzed product with a fixed molar ratio of (EG+PG)/PET 1, 2, 3 and 4

From Figure5-9, mole percent of BHET increased with depolymerization time while in Figure 5-10, mole percent of dimer decreased. Change of mole percent BHET and dimer with depolymerization time will interrupted with change of number average molecular weight in Figure 5-6. Molecular weight of BHET and dimer was 254 and 446, respectively, so BHET had smaller molecule than dimer. When PET was depolymerized for long time, glycolyzed product consisted of more amount of BHET but small amount of dimer, so number average molecular weight of glycolyzed product will be less too. Then, it can be concluded that depolymerization time was important to amount of BHET and dimer in glycolyzed product.

Figure 5-5 illustrated effect of depolymerization time on % free glycol of glycolyzed product. % Free glycol is determined by difference in weights of glycolyzed product before and after removal of free glycol. % Free glycol in this mean is the amount of unreacted EG and PG with PET chain. From Figure 5-5, it is found that %free glycol decreased with depolymerization times. From this results, it can be explained that the requirement of PET chain to EG and PG for chain scission is increased with depolymerization time, so the amount of EG and PG are reacted with PET chain is increased too, for this reason the amount of EG and PG unreacted is decreased.

5.1.3 Effect of molar ratio of (EG+PG)/PET

In this part, molar ratio of (EG+PG)/PET are varied to 1, 2, 3 and 4 with a fixed depolymerization time. Similar to section 5.1.2, hydroxyl value, % free glycol and number average molecular weight of glycolyzed product are determined for studying the effect of molar ratio of (EG+PG)/PET

The results of hydroxyl value of glycolyzed product before and after removal of free glycol, % free glycol and number average molecular weight are summarized in Table 5-4. Figure 5-11 and Figure 5-12 illustrate the effect of molar ratio of (EG+PG)/PET on hydroxyl value of glycolyzed product before and after

removal of free glycol. Effect of molar ratio of (EG+PG)/PET on % free glycol and number average molecular weight are shown in Figure 5-13 and Figure 5-14, respectively.

Table 5-4 Hydroxyl value , % free glycol and number average molecular weight of glycolyzed product at different molar ratio of (EG+PG)/PET at a fixed molar ratio of depolymerization time 1, 2, 4, 6 and 8 hrs

Depolymerization time (hrs)	Molar ratio of (EG+PG)/PET	Run	Hydroxyl value (mgKOH/g)		% Free glycol (%w/w)	Number average molecular weight
			Before extracted	After extracted		
1	1	gly1,1	612.73	223.14	38.12	502.82
	2	gly1,2	742.65	285.66	50.99	392.77
	3	gly1,3	817.06	341.27	55.75	328.29
	4	gly1,4	801.97	359.96	63.35	311.70
2	1	gly2,1	647.96	238.71	36.24	470.03
	2	gly2,2	781.05	333.48	50.08	336.45
	3	gly2,3	824.25	357.95	54.57	313.45
	4	gly2,4	841.67	393.28	63.16	285.29
4	1	gly4,1	719.09	276.39	31.03	405.95
	2	gly4,2	786.13	345.71	49.37	324.55
	3	gly4,3	830.70	382.05	51.59	293.68
	4	gly4,4	843.38	398.96	57.91	282.23
6	1	gly6,1	731.94	292.55	28.55	383.52
	2	gly6,2	809.72	355.35	49.75	315.74
	3	gly6,3	842.00	406.62	50.10	276.20
	4	gly6,4	851.65	420.33	55.71	266.93
8	2	gly8,1	736.99	307.10	28.71	365.35
	4	gly8,2	804.58	361.18	44.13	310.65
	6	gly8,3	869.52	419.61	50.84	267.39
	8	gly8,4	886.41	440.34	54.65	254.80

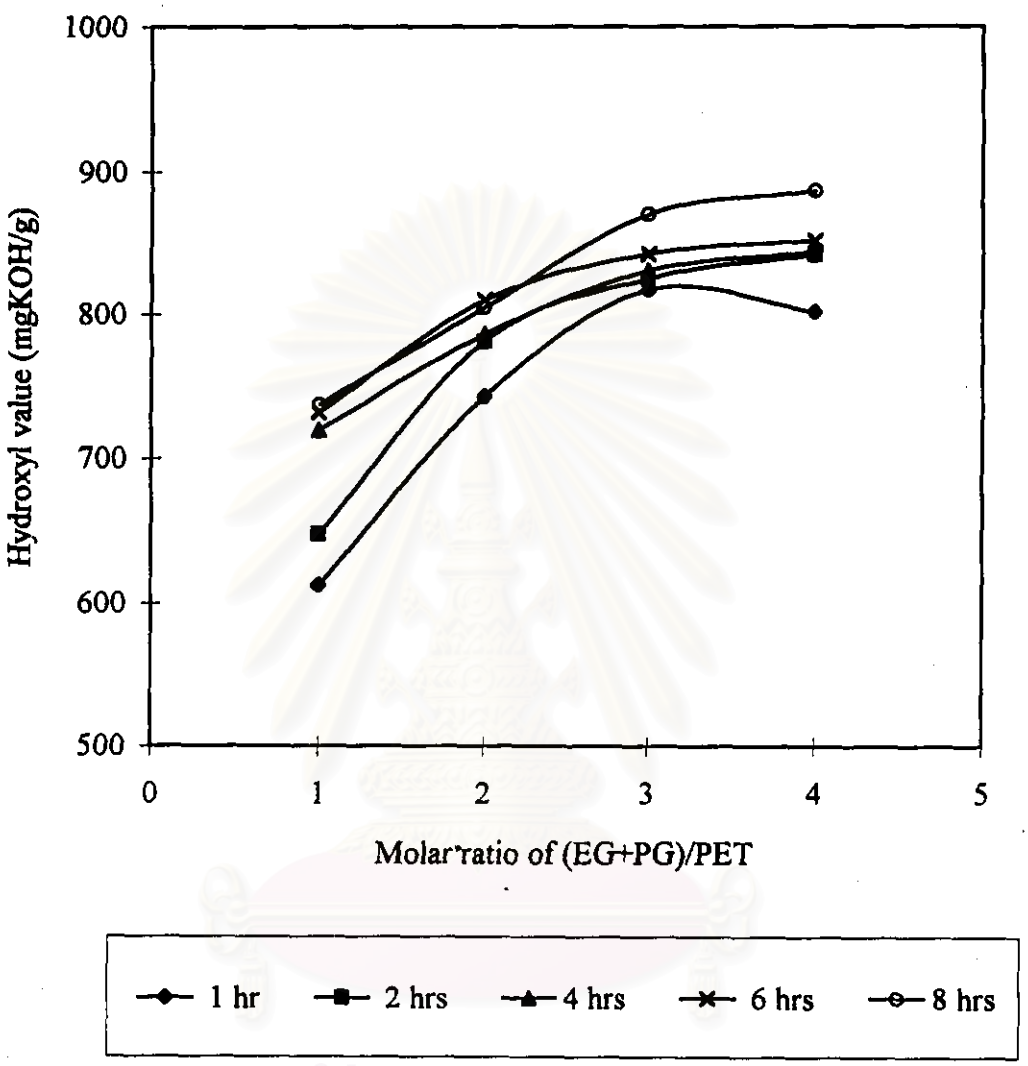

Figure 5-11 Effect of molar ratio of (EG+PG)/PET on hydroxyl value of glycolyze product before removal of free glycol with a fixed depolymerizatio times of 1, 2, 4, 6 and 8 hrs

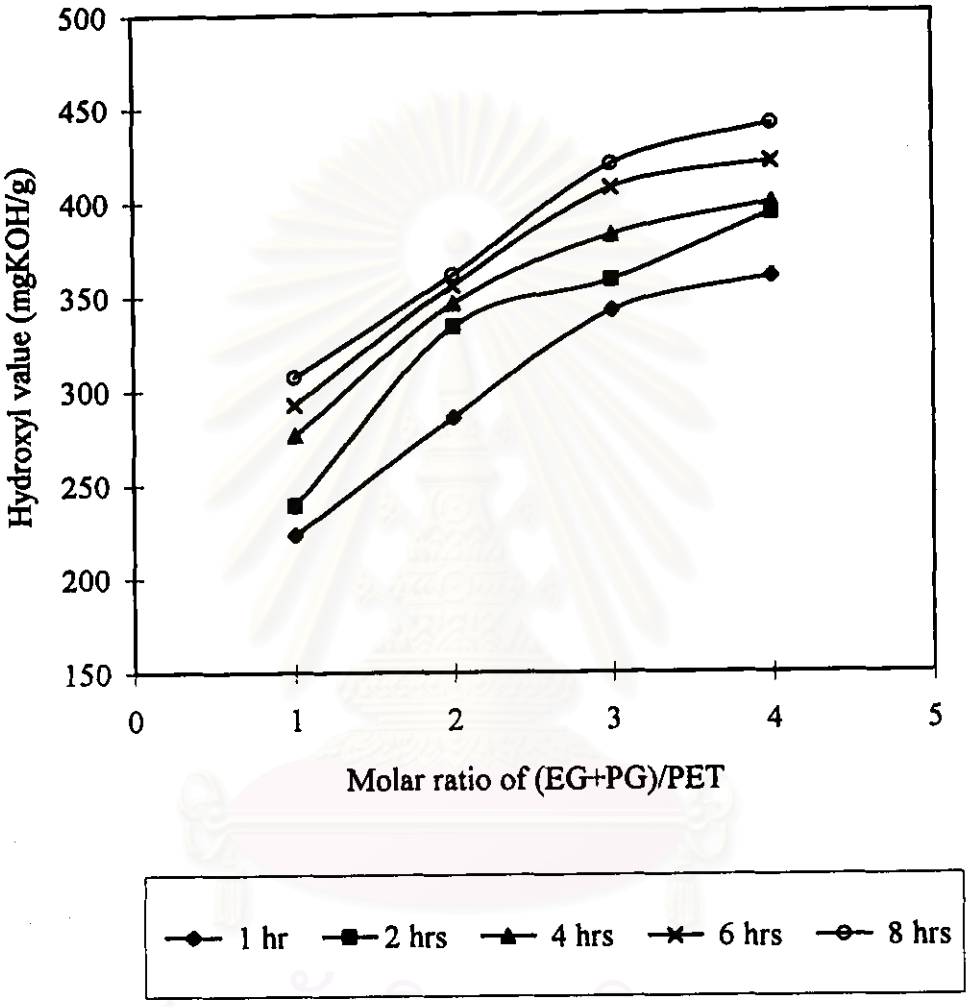

Figure 5-12 Effect of molar ratio of(EG+PG)/PET on hydroxyl value of glycolyzed product after removal of free glycol with a fixed depolymerization time of 1, 2, 4, 6 and 8 hrs

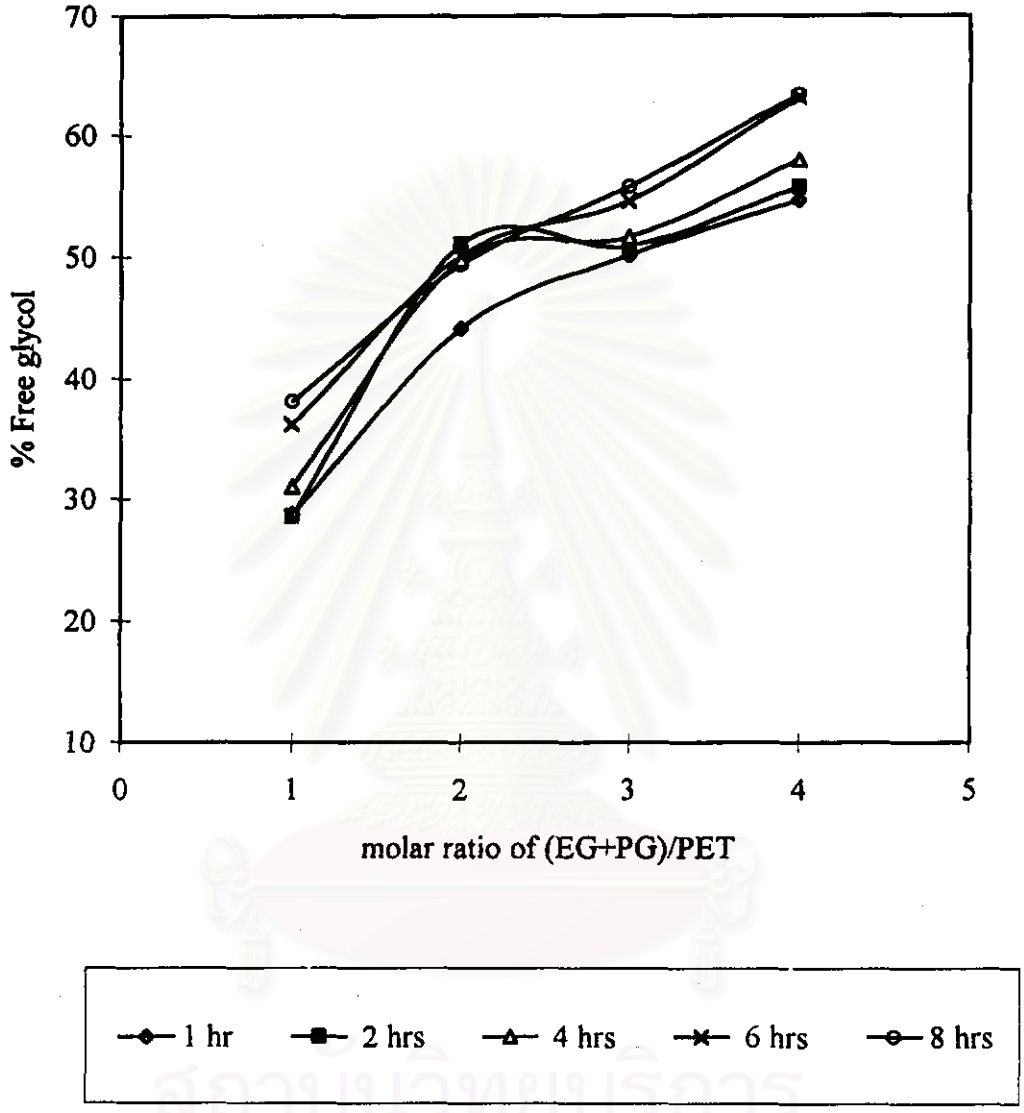

Figure 5-13 Effect of molar ratio of (EG+PG)/PET on percent free glycol of glycolyzed product with a fixed depolymerization times of 1, 2, 4, 6 and 8 hrs

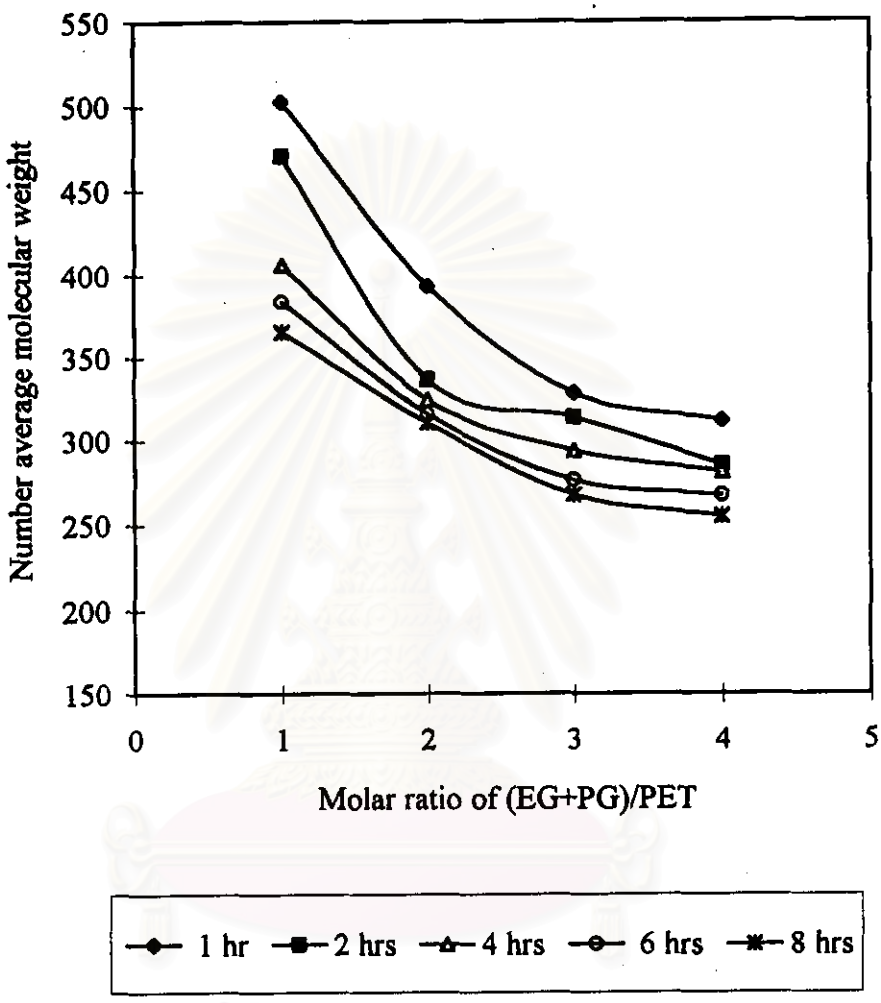

Figure 5-14 Effect of (EG+PG)/PET molar ratio on number average molecular weight of glycolyzed product with a fixed depolymerization times of 1, 2, 4, 6 and 8 hrs

From Figure 5-11 and Figure 5-12 at a fixed depolymerization time, hydroxyl value increased with molar ratio of (EG+PG)/PET. At low molar ratio of (EG+PG)/PET (1 to 2) hydroxyl value rapidly increase but at high molar ratio of (EG+PG)/PET (>2 to 4) hydrioxyl value increase slower than at low molar ratio. At molar ratio of (EG+PG)/PET is 1, the amount of EG and PG was not sufficient for cutting PET chain into short chains. Therefore, product obtained was a mixture of short and long chains molecules. When more EG and PG was added at molar ratio of (EG+PG)/PET is 2, this ratio is excess with PET. EG and PG reacted with long chains PET to cut them to short chains PET. Mostly of product obtained from this molar ratio will consisted short and small molecules. In case of adding more EG and PG (> molar ratio of (EG+PG)/PET is 2) , EG and PG will react with long chain PET that remained in mixture, because of in mixture consisted less amount of long chain PET, then increasing of short chain PET will not be as much as that at low molar ratio of (EG+PG)/PET. Then from this reason, it corresponse to the results in Figure 5-14, number average molecular weight decreased with molar ratio of (EG+PG)/PET.

From Table 5-2, at different molar ratio (EG+PG)/PET, effect of molar ratio of (EG+PG)/PET on initial rate of depolymerization is shown in Table 5-5 and Figure 5-15.

Table 5-5 Initial rate of depolymerization at various molar ratio of (EG+PG)/PET

Molar ratio of (EG+PG)/PET	Initial rate (Hydroxyl value/hr)
1	460
2	767
3	1045
4	1343

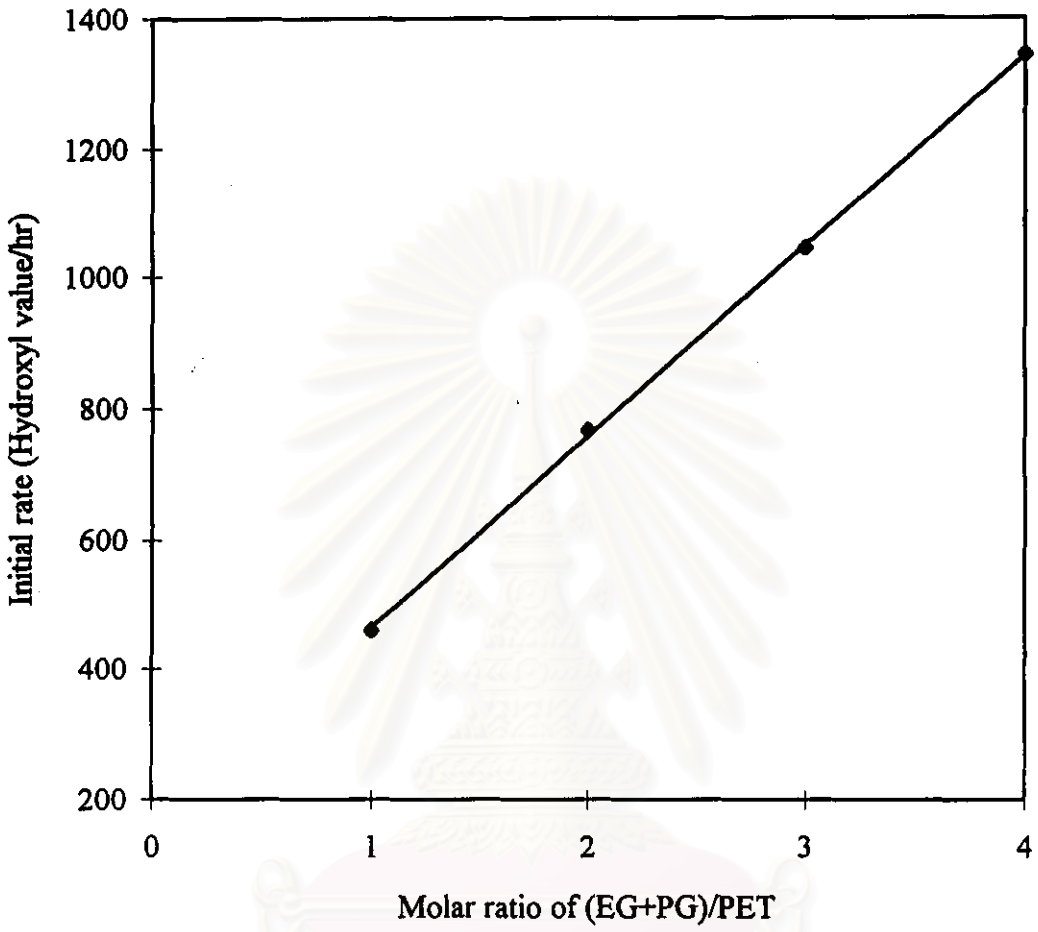

Figure 5-15 Initial rate of PET depolymerization under different molar of (EG+PG)/PET

From Figure 5-15, increasing of initial rate is shown to be a linear relationship with increasing of molar ratio of (EG+PG)/PET. Based on these kinetics, it is believed that the depolymerization of PET is dependent on EG and PG. Because the scission reaction (5-1) happened so quickly and randomly, the oligomer higher than dimer are too minute to be detected in the case of high molar ratio of (EG+PG)/PET. However, in a low molar ratio of (EG+PG)/PET, glycolyzed product consisted of oligomer, having a higher molecular weight.

From Table 5-3 at a fixed depolymerization time, effect of molar ratio of (EG+PG)/PET to mole percent of BHET and dimer are shown in Figure 5-16 and Figure 5-17, respectively.

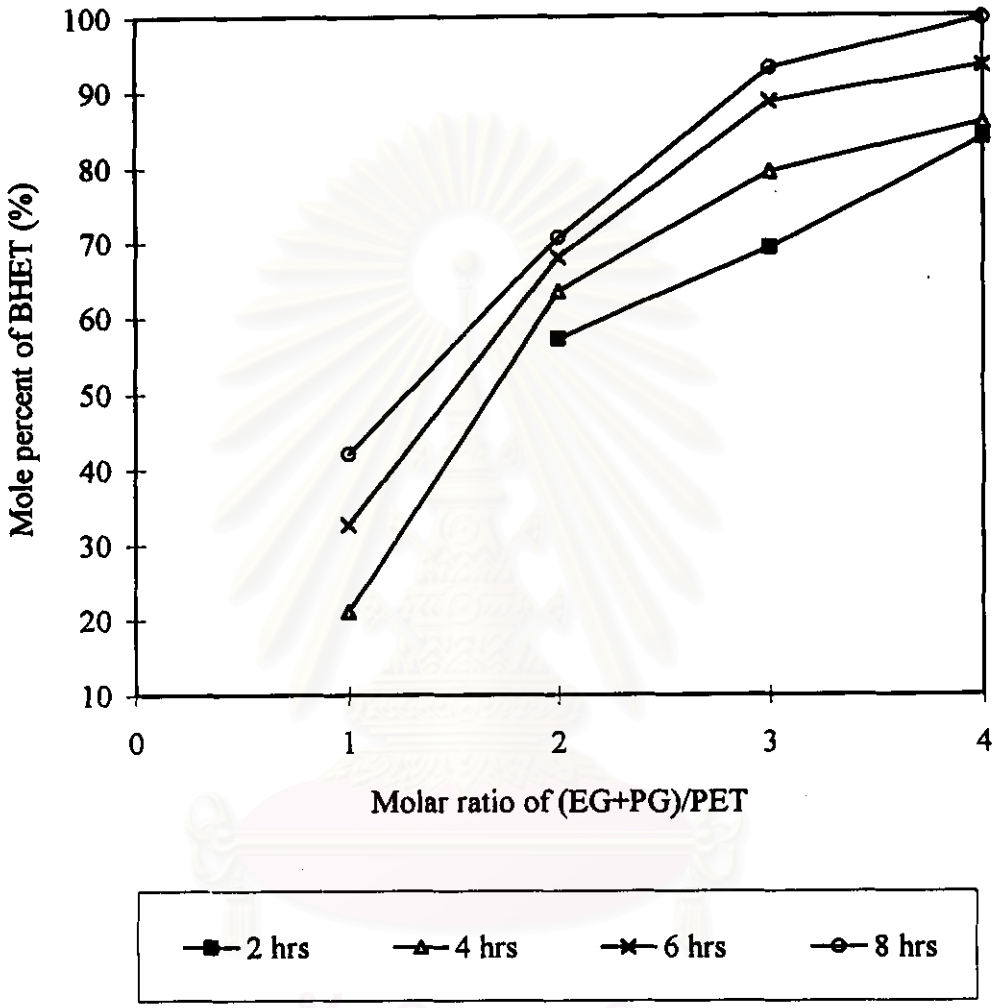

Figure 5-16 Effect of molar ratio of (EG+PG)/PET on mole percent of BHET in glycolyzed product with a fixed depolymerization time of 2, 4, 6 and 8 hrs

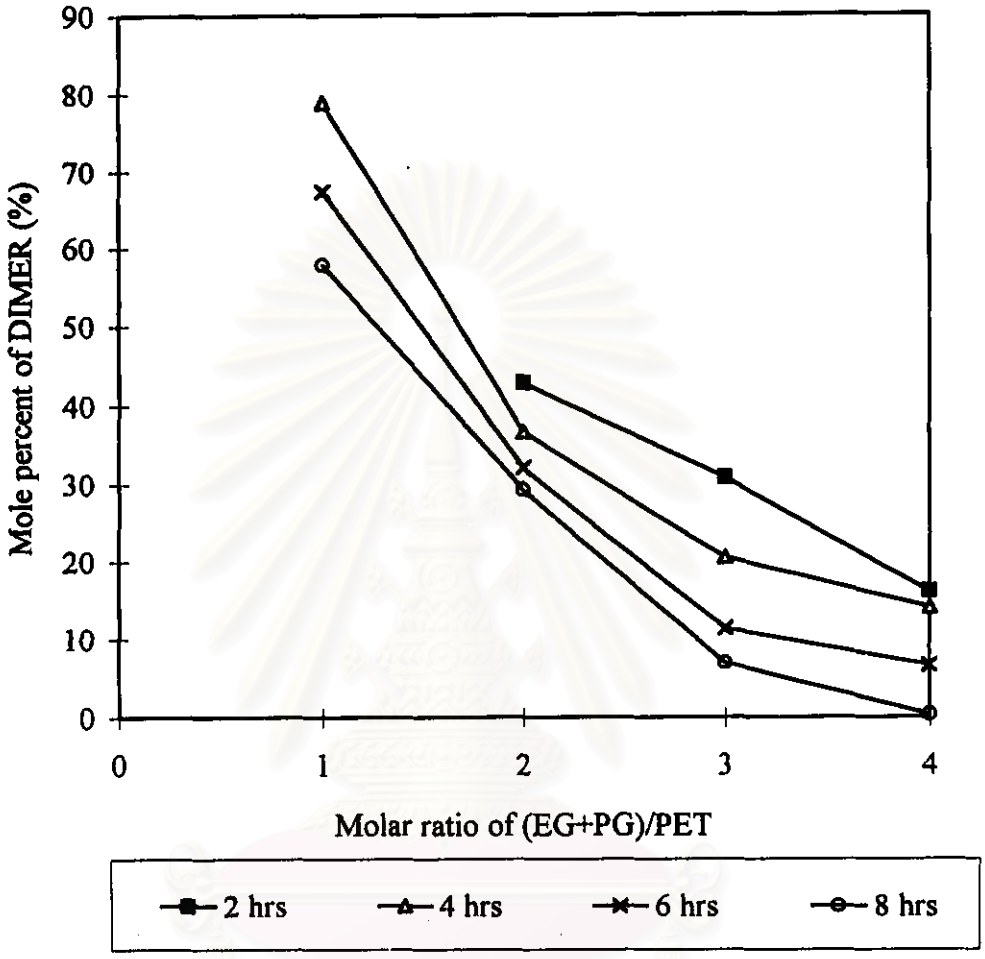

Figure 5-17 Effect of molar ratio of (EG+PG)/PET on mole percent of DIMER in glycolyzed product with a fixed depolymerization time of 1, 2, 4, 6 and 8 hrs

From Figure 5-16 and Figure 5-17, mole percent of BHET increased with molar ratio of (EG+PG)/PET but mole percent of dimer decreased, this indicated that amount of EG and PG is important to depolymerized PET to obtained a predominant amount of BHET or dimer in the glycolyzed product [10].

5.1.4 Identification of glycolyzed product

Identification of glycolyzed product was done by using spectroscopic method, with Fourier Transformed Infrared Spectroscopy (FT-IR).

Glycolyzed product chosen for FT-IR run was prepared by using molar ratio of (EG+PG)/PET is 4 and depolymerization time 4 hrs (run gly4,4), so that glycolyzed product would consist mostly of BHET. The IR spectroscopy absorption band of this glycolyzed product was, then, used to represent that of BHET.

In chemical structure of BHET (Figure 5-18) consisted of many functional groups and chemical bonds. Each of functional group and chemical bond will showed absorption band or peak at different absorption frequency. In Figure 5-19, illustrated FT-IR spectrum of glycolyzed product, absorption bands or peaks of glycolyzed product are listed in Table 5-6.

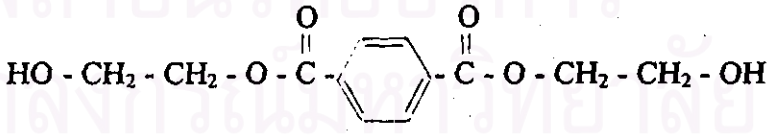

Figure 5-18 Chemical structure of BHET

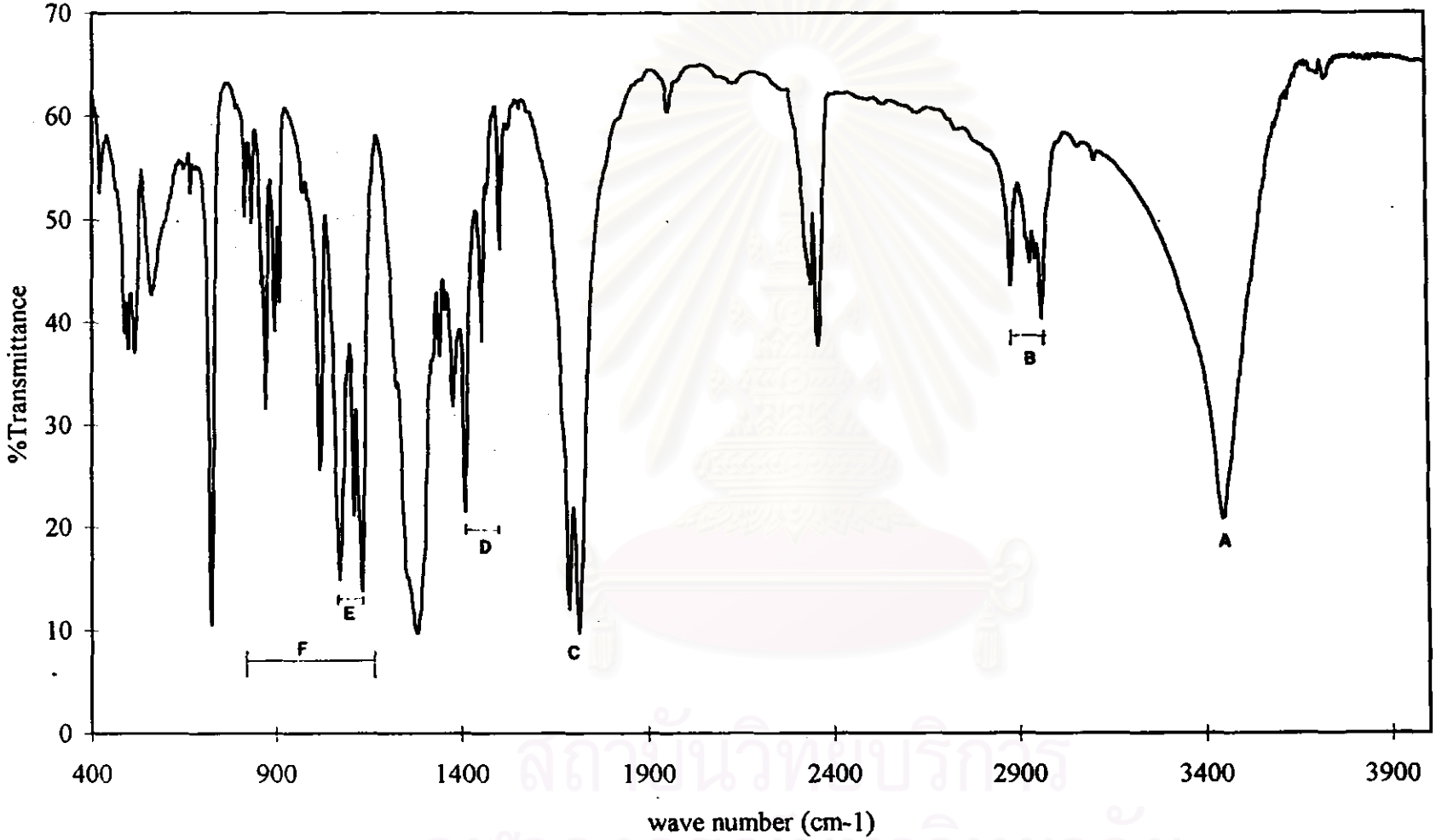

Figure 5-19 Infrared spectroscopy of glycolyzed product after removal of free glycol

Table 5-6 Absorption frequencies of fuctional groups and chemical bonds on glycolyzed product [17], [18].

Position	Absorption frequencies (cm^{-1})	Group	Remarks
A	3400	- OH	Sharp, O-H stretching
B	2800-3000	C - H	C - H stretching
C	1650-1700	C = O	C = O stretching
D	1400-1500	Aromatic ring	This is usually the strongest of the two or theree bands
E	1100-1300	C - O	Usually two strong bands due to C - O stretching
F	800-1200	C - C	C - C stretching

All groups in Table 5-6 are interrupted with chemical structure of BHET and this infrared spectrum is similar to infrared spectrum of pure BHET that is studied by J.Y.Chen et al. (Figure 5-20) [10].

The difference between Figure 5-19 and Figure 5-20 is some absorption bands in Figure 5-19 do not exist in Figure 5-19. It can be discussed that BHET in this experiment is not pure. There may be additive or other chemical substance present in BHET solution. FT-IR does not differentiate BHET and dimer because of BHET and dimer consist of the same functional groups.

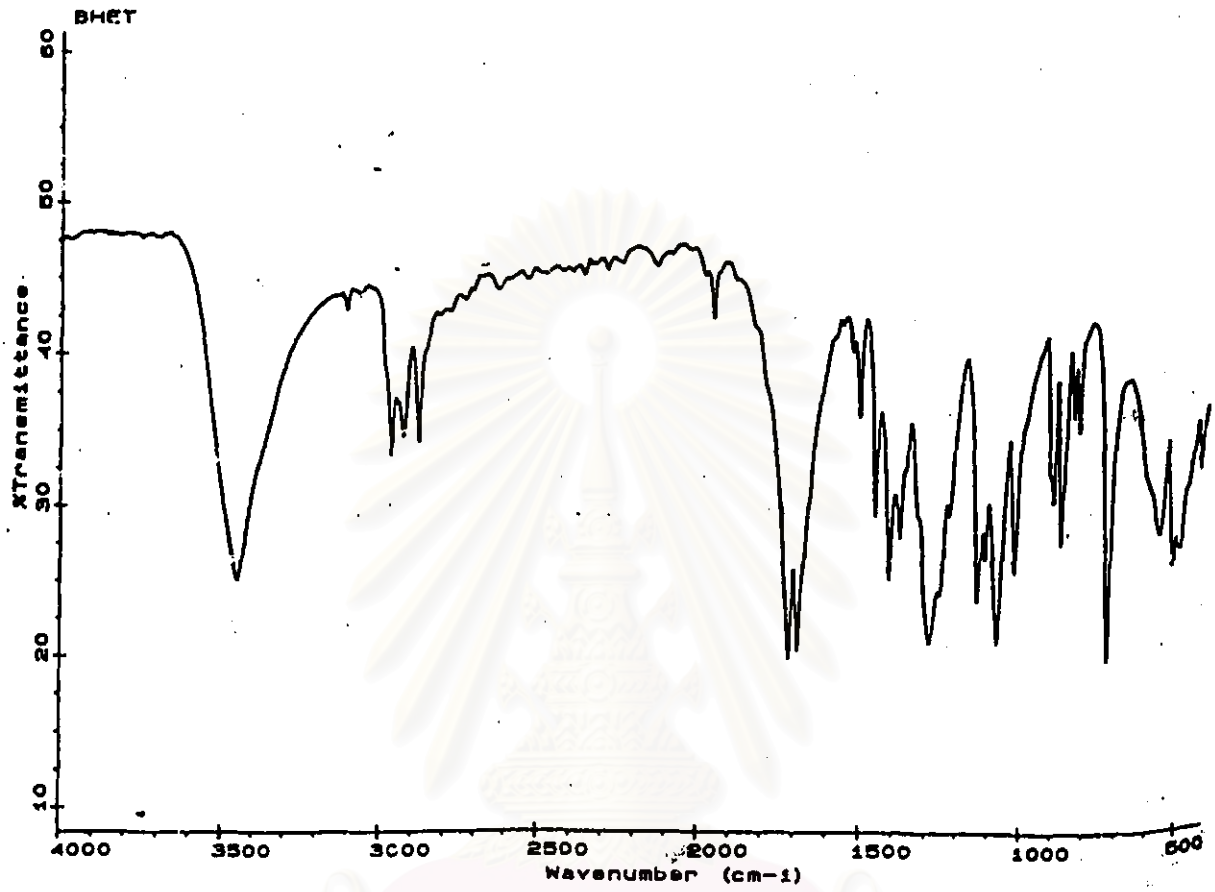

Figure 5-20 Infrared spectroscopy of BHET [10]

5.2 SYNTHESIS OF UNSATURATED POLYESTERS

5.2.1 Unsaturated polyester

Unsaturated polyester was prepared from glycolyzed product before removal of free glycol as diol and maleic acid as diacid, catalyst was not used in this experiment. During reaction time, acid value of unsaturated polyester was monitored to follow the reaction. The acid value of final unsaturated polyester dropped to 50 ± 2 mgKOH/g. Then, hydroquinone was added in order to inhibit the resin and so prevented premature gelation when the styrene was added [6]. When the batch temperature fall to 90 ^{o}C , styrene monomer was added. The temperature of styrene-addition is important because if a temperature lower than 90 ^{o}C is used, the viscosity of the resin will be too high for the styrene to blend in rapidly. If the temperature exceed 90 ^{o}C , styrene monomer may be polymerized to polystyrene [6]. The resulting liquid of unsaturated polyester resin will have a pale straw color and high viscosity. Liquid unsaturated polyester resin was shown in Figure 5-21.

In order to test mechanical properties, liquid unsaturated polyester resin was casted by used methyl ethyl ketone peroxide as catalyst and curing conditions was 1 hr at 100 ^{o}C and following 2 hrs at 80 ^{o}C. Casted unsaturated polyester was shown in Figure 5-22. From experiment, it is found that, the right amount of catalyst and temperature were necessary to cast unsaturated polyesters. If either more catalyst or higher temperature is used, unsaturated polyester liquid will rapidly set to solid resin, resulting in crack on surface and inside casted resin. If either smaller amount of catalyst or lower temperature is used, unsaturated polyester liquid will require more time for setting to solid.

Figure 5-21 Unsaturated polyester liquid synthesized from PET bottles

Figure 5-22 Casted unsaturated polyester synthesized from PET bottles

5.2.2 Mechanical properties of unsaturated polyester

In this study, mechanical properties of unsaturated polyesters analyzed are impact strength and hardness. Impact strength is determined by using Izod impact type and hardness is analyzed by shore durometer scale D (shore D). Effect of depolymerization time and molar ratio of (EG+PG)/PET on mechanical properties of unsaturated polyesters were studied in this experiment.

5.2.2.1 *Effect of depolymerization time on impact strength and hardness*

The results of impact strength and hardness of unsaturated polyesters effected by depolymerization time is shown in Table 5-7.

Figure 5-23 showed effect of depolymerization time of glycolyzed product on impact strength of unsaturated polyester. From Figure 5-23, impact strength of unsaturated polyester increases with depolymerization time of glycolyzed product. Prior to section 5.1.2, PET was depolymerized by using long

Table 5-7 Results of impact strength and hardness of unsaturated polyesters synthesized from glycolyzed product are effected by depolymerization time

Molar ratio of (EG+PG)/PET	Depolymerization time (hrs)	Run	Average Impact strength (J)	Hardness (Shore D)
1	1	UPGLY1,1	4.788	46.83
	2	UPGLY2,1	4.830	48.33
	4	UPGLY4,1	4.840	52.00
	6	UPGLY6,1	4.870	66.67
	8	UPGLY8,1	4.894	78.67
2	1	UPGLY1,2	4.840	74.50
	2	UPGLY2,2	4.864	78.17
	4	UPGLY4,2	4.876	82.50
	6	UPGLY6,2	4.890	82.33
	8	UPGLY8,2	4.980	83.50
3	1	UPGLY1,3	4.880	74.00
	2	UPGLY2,3	4.920	76.67
	4	UPGLY4,3	4.940	75.00
	6	UPGLY6,3	4.980	80.33
	8	UPGLY8,3	5.058	81.33
4	1	UPGLY1,4	4.914	64.83
	2	UPGLY2,4	4.940	67.83
	4	UPGLY4,4	4.950	75.83
	6	UPGLY6,4	5.004	80.00
	8	UPGLY8,4	5.490	81.50

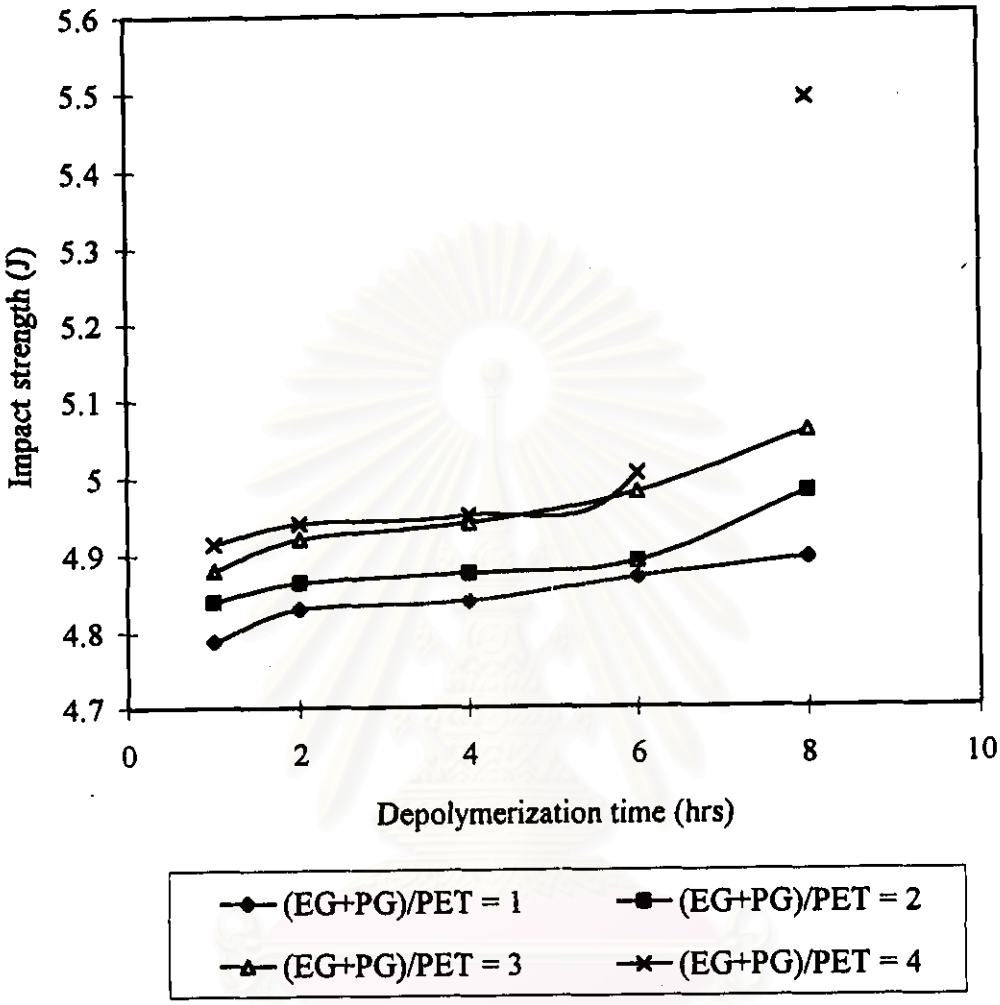

Figure 5-23 Effect of depolymerization times on impact strength of unsaturated polyesters with a fixed (EG+PG)/PET molar ratio of 1, 2, 3 and 4

depolymerization time, glycolyzed product will consisted short-chain molecules, BHET, and consisted less amount of dimer. Consider Table 5-3, For example, at fixed molar ratio of (EG+PG)/PET 1:3, it is found that mole percent of BHET increased with depolymerization time, so the amount of BHET in glycolyzed product run gly8,3 > gly6,3 > gly4,3 > gly2,3 >gly1,3. When they were used as raw material of unsaturated polyester, they would reacted with maleic acid, hydroxyl group from glycolyzed product is reacted with carboxyl group from maleic acid, from this reaction it brought to form ester group and unsaturated group (double bond) in polymer chain. Mechanism of reaction between glycolyzed product and maleic acid is shown in Figure 5-24

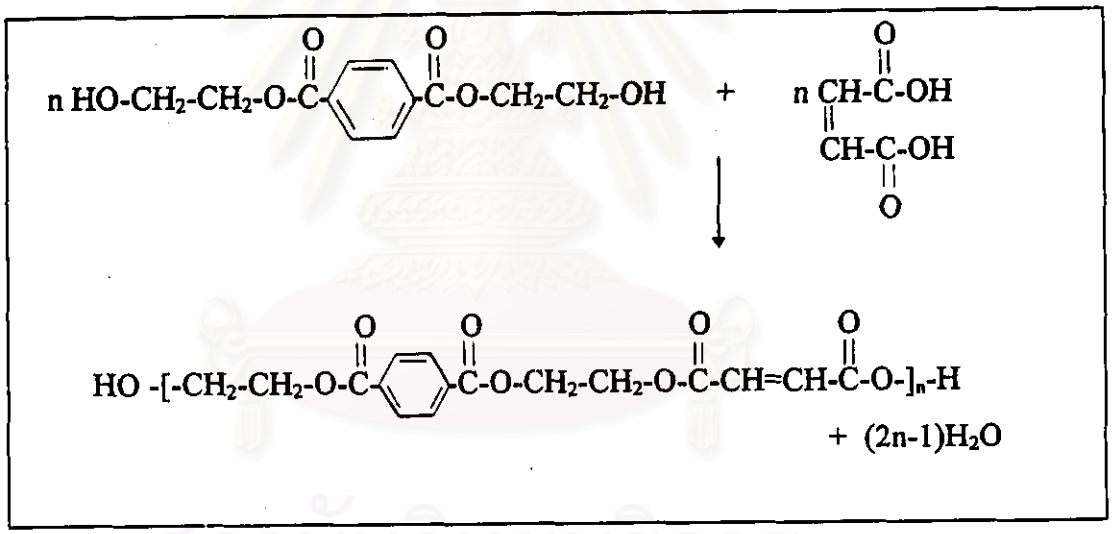

Figure 5-24 Mechanism of reaction between glycolyzed product and maleic acid

From mechanism in Figure 5-24, if in glycolyzed product consisted more amount of short-chain molecule, in polymer chain will consisted more amount of unsaturated group, when polyester chain cross-linked with styrene monomer, cross-linking may occurred at many position. When, unsaturated polyester is synthesized from gly8,3 cross-linking occurred more than the case of gly6,3, gly4,3, gly2,3 and gly1,3. Or it can be say that unsaturated polyester synthesized from glycolyzed product with long depolymerized time will have cross-linking more than the

glycolyzed product with long depolymerized time will have cross-linking more than the case of short time of depolymerization. Unsaturated polyester consisted of more cross-linking, its impact strength was higher. So, it can be concluded that unsaturated polyester synthesized from long depolymerization time -glycolyzed product will have higher impact strength.

The results of hardness of unsaturated polyesters are effected by depolymerization time are shown in Figure 5-25. From Figure 5-25, hardness of unsaturated polyester increased with depolymerization time of glycolyzed product. By the same reason given in impact strength, unsaturated polyester synthesized from long depolymerization time-glycolyzed product consisted of many double bond that will provide cross-linking in polymer chain. Then polymer chain will be stronger when high degree of cross linking occurred.

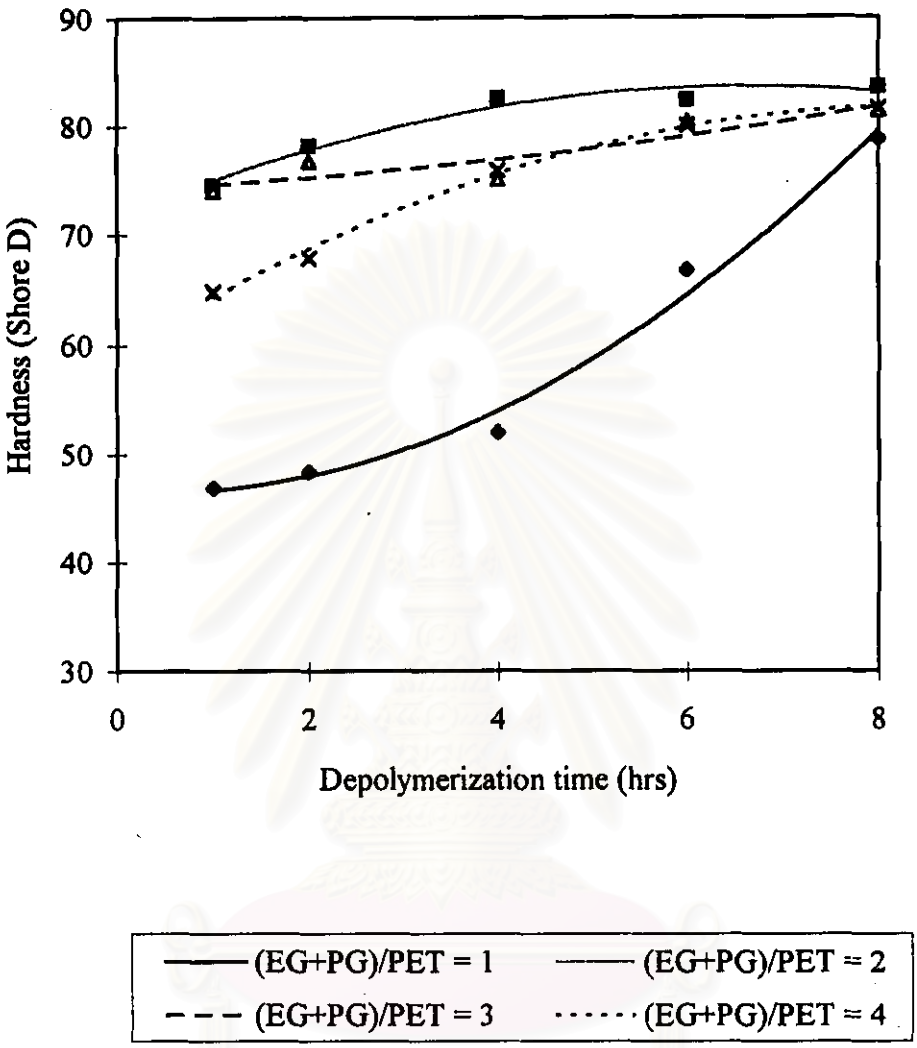

Figure 5-25 Effect of depolymerization times on hardness of unsaturated polyester synthesized from glycolyzed product with a fixed molar ratio of (EG+PG)/PET 1, 2, 3 and 4

5.2.3.2 *Effect of molar ratio of (EG+PG)/PET on impact strength and hardness*

The results of impact strength and hardness of unsaturated polyesters effected by molar ratio of (EG+PG)/PET is shown in Table 5-8.

Figure 5-26 shows effect of molar ratio of (EG+PG)/PET of glycolyzed product on impact strength of unsaturated polyesters. From Figure 5-26, impact strength of unsaturated polyesters increase with molar ratio of (EG+PG)/PET of glycolyzed product. The reason is that, from Figure 5-16 and Figure 5-17, mole percent of BHET increased with molar ratio of (EG+PG)/PET but dimer decreased, so similar to section 5.2.2.1 increasing of impact strength with molar ratio of (EG+PG)/ PET is effected from cross-linking of unsaturated polyesters. The other factor that effected impact strength is EG and PG remained in glycolyzed product. Glycolyzed product before removal of free glycol is used as raw material, in that way EG and PG will mixed with glycolyzed product. From Figure 5-13, %free glycol increase with molar ratio of (EG+PG)/PET, then at high molar ratio of (EG+PG)/PET, there are more amount of mixed glycol (EG and PG) in glycolyzed product. Mixed glycol in glycolyzed product will increase impact strength by reacting with maleic acid to form ester group and cross-linked with styrene, so that degree of cross-linking in unsaturated polyester increased.

Table 5-8 Results of impact strength and hardness of unsaturated polyesters synthesized from glycolyzed product are effected by molar ratio of (EG+PG)/PET

Depolymerization Time (hrs)	Molar ratio of (EG+PG)/PET	Run	Average Impact strength (J)	Hardness (Shore D)
1	1	UPGLY1,1	4.788	46.83
	2	UPGLY1,2	4.840	74.50
	3	UPGLY1,3	4.880	74.00
	4	UPGLY1,4	4.914	64.83
2	1	UPGLY2,1	4.830	48.33
	2	UPGLY2,2	4.864	78.17
	3	UPGLY2,3	4.920	76.67
	4	UPGLY2,4	4.940	67.83
4	1	UPGLY4,1	4.840	52.00
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	3	UPGLY4,3	4.940	75.00
	4	UPGLY4,4	4.950	75.83
6	1	UPGLY6,1	4.870	66.67
	2	UPGLY6,2	4.890	82.33
	3	UPGLY6,3	4.980	80.33
	4	UPGLY6,4	5.004	80.00
8	1	UPGLY8,1	4.894	78.67
	2	UPGLY8,2	4.980	83.50
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	4	UPGLY8,4	5.490	81.50

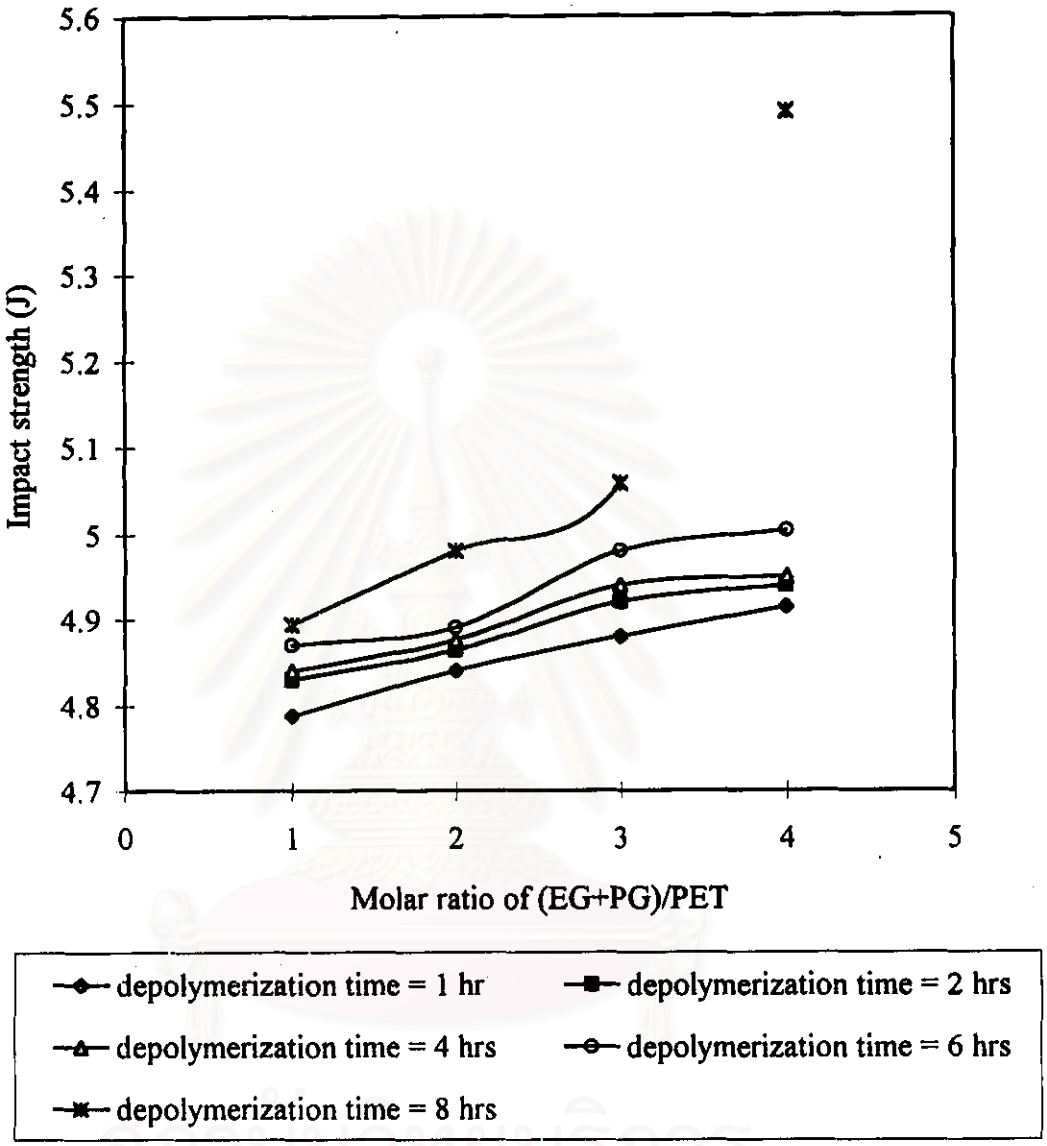

Figure 5-26 Effect of molar ratio of (EG+PG)/PETon impact strength of unsaturated polyesters with a fixed depolymerization time of 1, 2, 4, 6 and 8 hrs

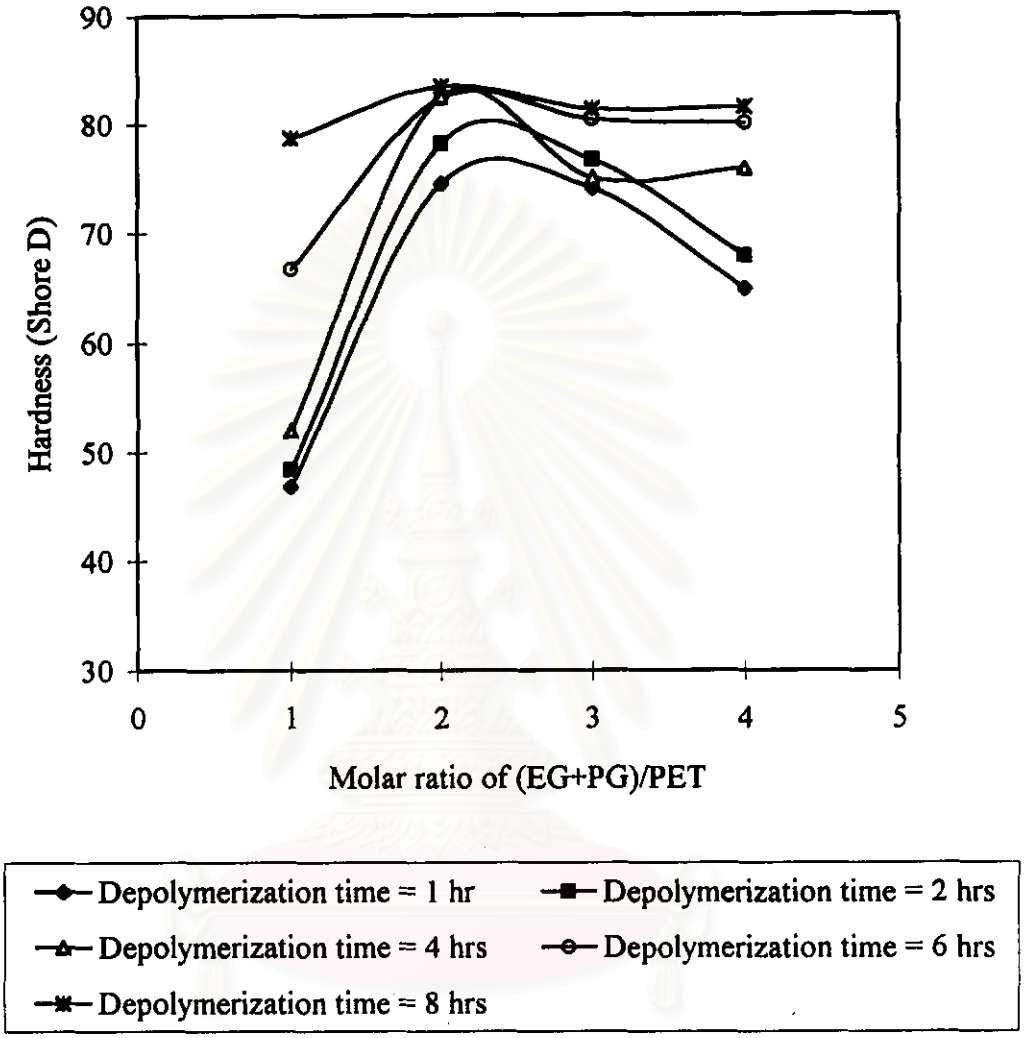

Figure 5-27 Effect of (EG+PG)/PET molar ratio on hardness of unsaturated polyesters synthesized from glycolyzed product with a fixed depolymerization time at 1, 2, 4, 6 and 8 hrs

Effect of molar ratio of (EG+PG)/PET of glycolyzed product on hardness of unsaturated polyester is illustrated in Figure 5-27. From Figure 5-27, hardness will increase from molar ratio 1 to 2, after that hardness decreased with higher molar ratio(> 2 to 4). Consider at low molar ratio of (EG+PG)/PET, glycol remained in glycolyzed product in this molar ratio less than glycolyzed product at high molar ratio, some of glycol may be reacted with maleic acid to form ester group and cross-linked, then net amount of glycol in unsaturated polyester will less than glycol in glycolyzed product at high molar ratio, ester group and cross-link lead to higher hardness. Owing to more amount of glycol is mixed with glycolyzed product at higher molar ratio of (EG+PG)/PET, ester group and unsaturated group may occured by reaction between glycol and maleic acid. In case of excess glycol ,the unreacted glycol may mixed with unsaturated polyester that cause it to behave as flexible part of polymer. From this reason, hardness of unsaturated polyester synthesized from glycolyzed product is using high molar ratio of (EG+PG)/PET will decrease.