CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Glycolysis of Foam

Rigid polyurethane foam can be broken down through glycolysis at temperature of 130 to150°C by diethanolamine with sodium hydroxide as a catalyst into clear brown viscous liquid. The glycolysis of polyurethane was found as shown in Figure 4.1 [19].
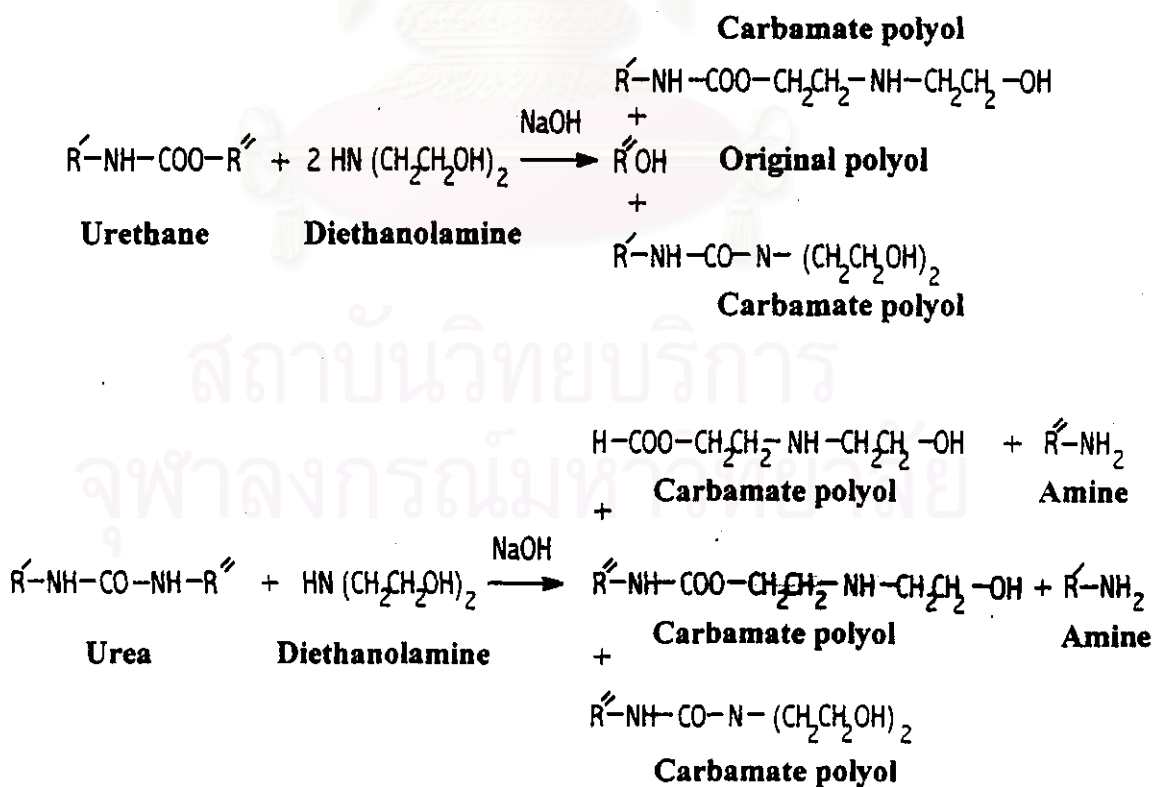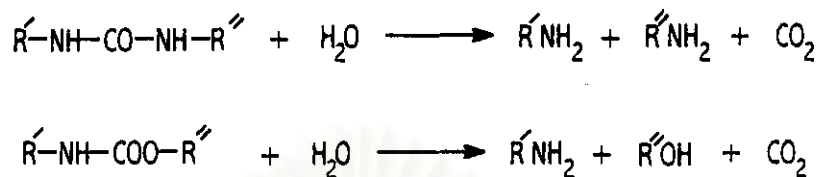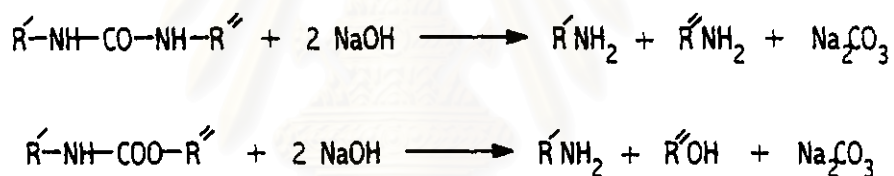

Figure 4.1 The decomposition of rigid polyurethane foam by diethanolamine

Any water present will react with urethane and urea groups according to Figure 4.2

$$R'-NH-CO-NH-R'' \ + \ H_2O \ \longrightarrow \ R'NH_2 \ + \ R''NH_2 \ + \ CO_2$$

$$R'-NH-COO-R'' \ + \ H_2O \ \longrightarrow \ R'NH_2 \ + \ R''OH \ + \ CO_2$$

Figure 4.2 Reaction of urethane and urea groups with water

Sodium hydroxide will also react according to the scheme shown in Figure 4.3

$$R'-NH-CO-NH-R'' \ + \ 2 \ NaOH \ \longrightarrow \ R'NH_2 \ + \ R''NH_2 \ + \ Na_2CO_3$$

$$R'-NH-COO-R'' \ + \ 2 \ NaOH \ \longrightarrow \ R'NH_2 \ + \ R''OH \ + \ Na_2CO_3$$

Figure 4.3 Reaction of urethane and urea groups with sodium hydroxide

IR spectra of the rigid polyurethane foam, diethanolamine and the glycolyzed products are illustrated by Figures 4.4 to 4.8. GP11, GP21 and GP31 refer to the glycolyzed products obtained from glycolysis with foam to diethanolamine weight ratios of 1 to 1, 2 to 1, and 3 to 1, respectively.
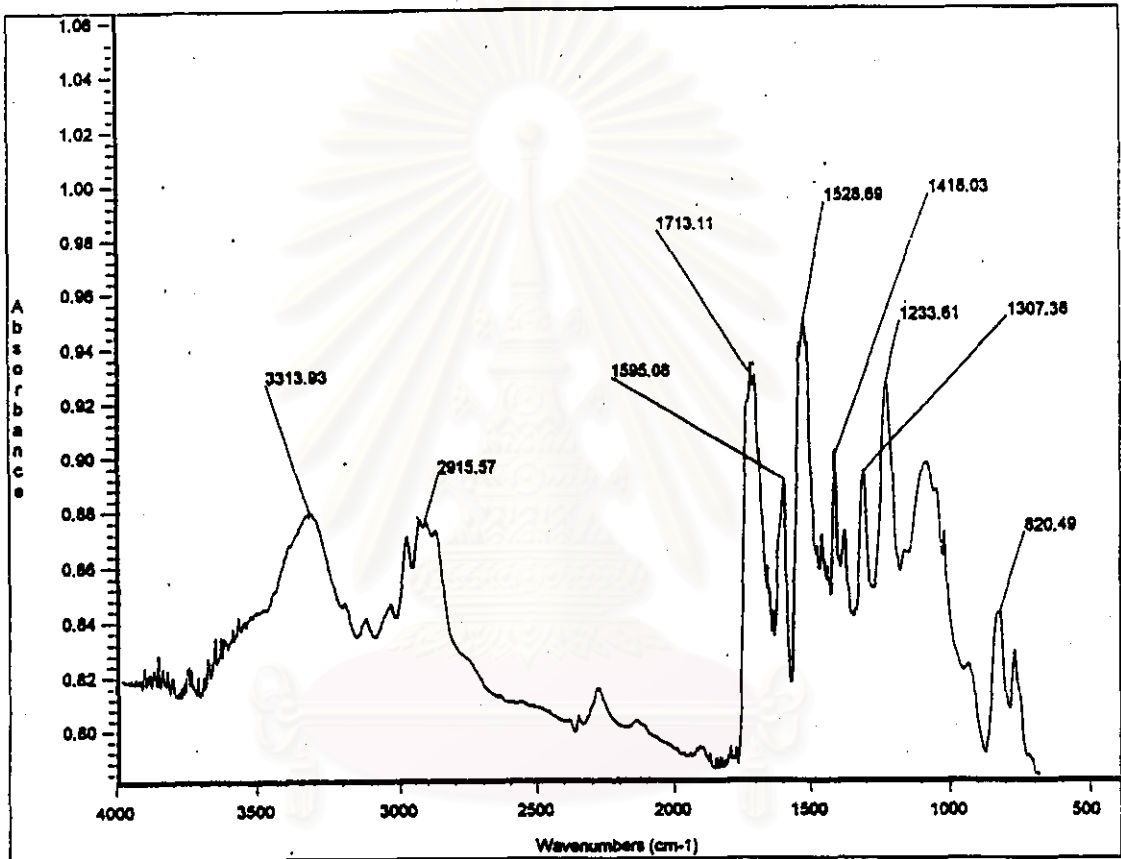
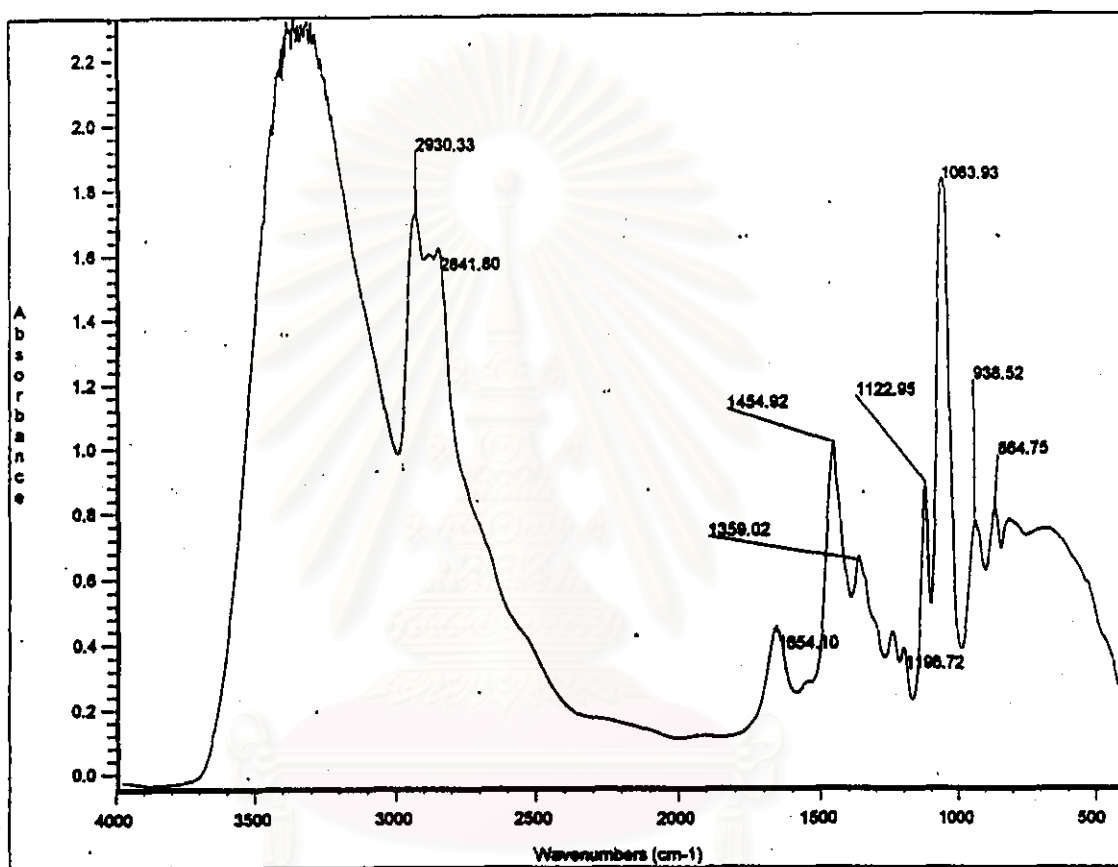**Figure 4.4** IR spectrum of the rigid polyurethane foam
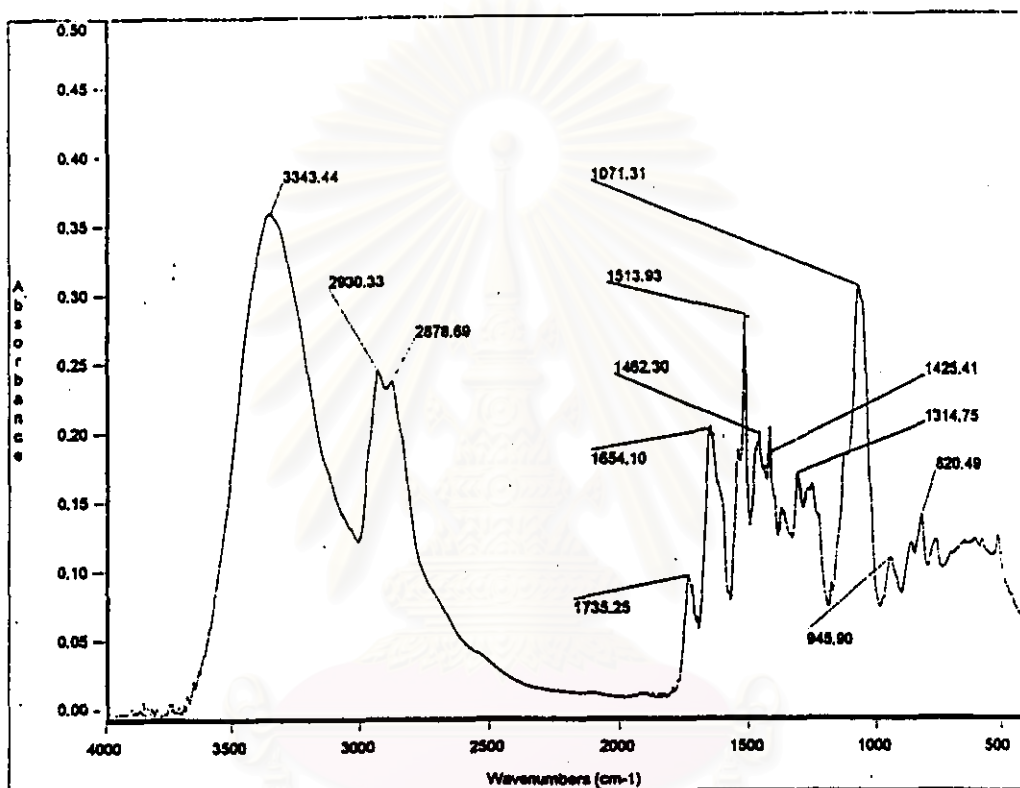
Figure 4.5 IR spectrum of diethanolamine

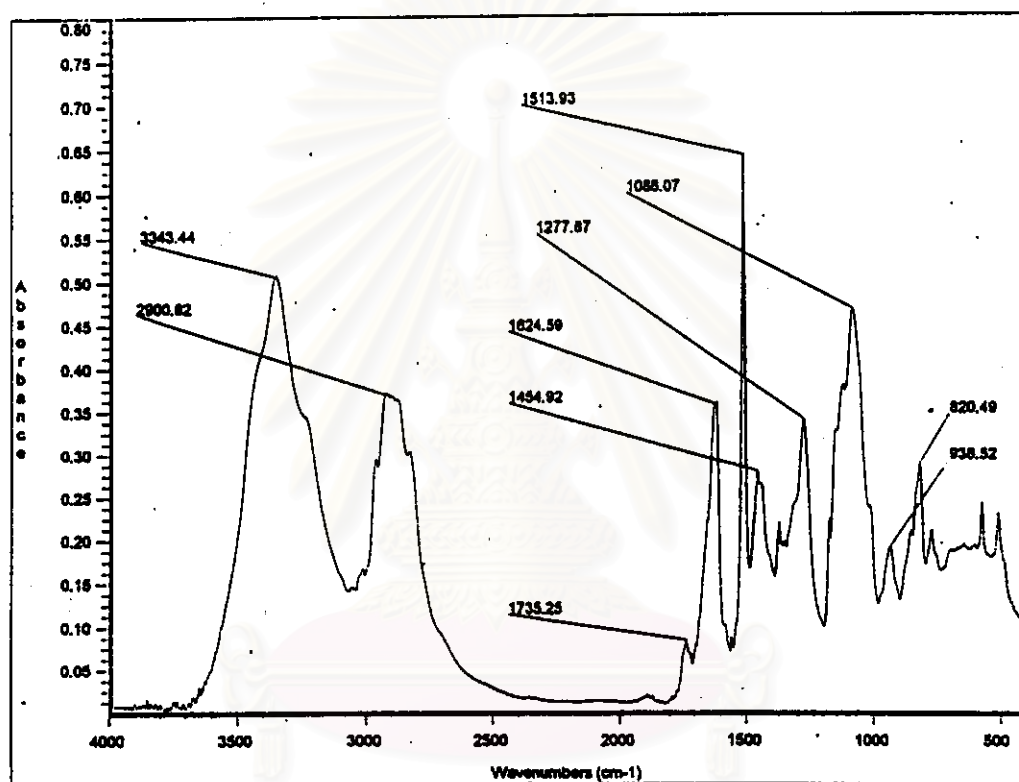**Figure 4.6** IR spectrum of the glycolyzed product (GP 11)

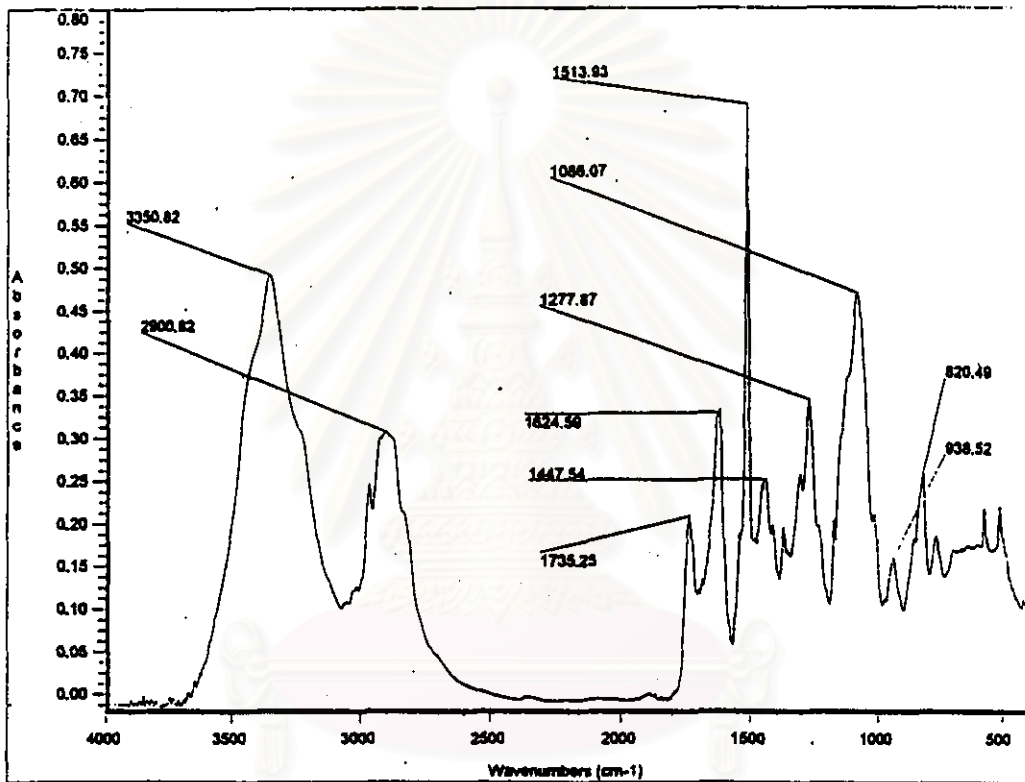**Figure 4.7** IR spectrum of the glycolyzed product (GP 21)

Figure 4.8 IR spectrum of the glycolyzed product (GP 31)

IR spectra of the glycolyzed products are compared with those of foam and diethanolamine. It is found that, after the decomposition was carried out, there are noticable changes in some peaks. These changes agree with the decomposition scheme shown in Figures 4.1 to 4.3.

IR spectra of the glycolyzed products are compared with that of diethanolamine. It can be seen that in each spectrum of the glycolyzed products, a significant increase of the peak at around 1654 cm^{-1} is found. This peak is resulted from N-H bending of primary amines produced by the chemical decomposition of urethane and urea linkages.

IR spectra of the glycolyzed products are also compared with that of the foam using the peak at 820 cm^{-1} as a standard. This peak is assigned as the peaks of aromatic ring composed in the chemical structure of polyurethane foam. It is clear that the peak at around 1,730 cm^{-1}, which is assigned as the peak of carbonyl group of urethane, decreases significantly. The decrease of these peaks indicates the break down of urethane and urea groups.

A minor phase separation of the glycolyzed products was observed after a few days at room temperature. The clear top layer liquid was characterized to be polyol by IR spectroscopy.

According to IR results, it can be concluded that urethane and urea groups in polyurethane foam are consumed in the decomposition reaction. Primary amines are produced and polyols are generated during the decomposition process.

Glycolyzed products were characterized by ¹H NMR spectroscopy. The ¹H NMR spectra of GP11 and GP31 are shown in Figures 4.9 and 4.10. ¹H NMR spectrum of GP21 is similar to that of GP31.

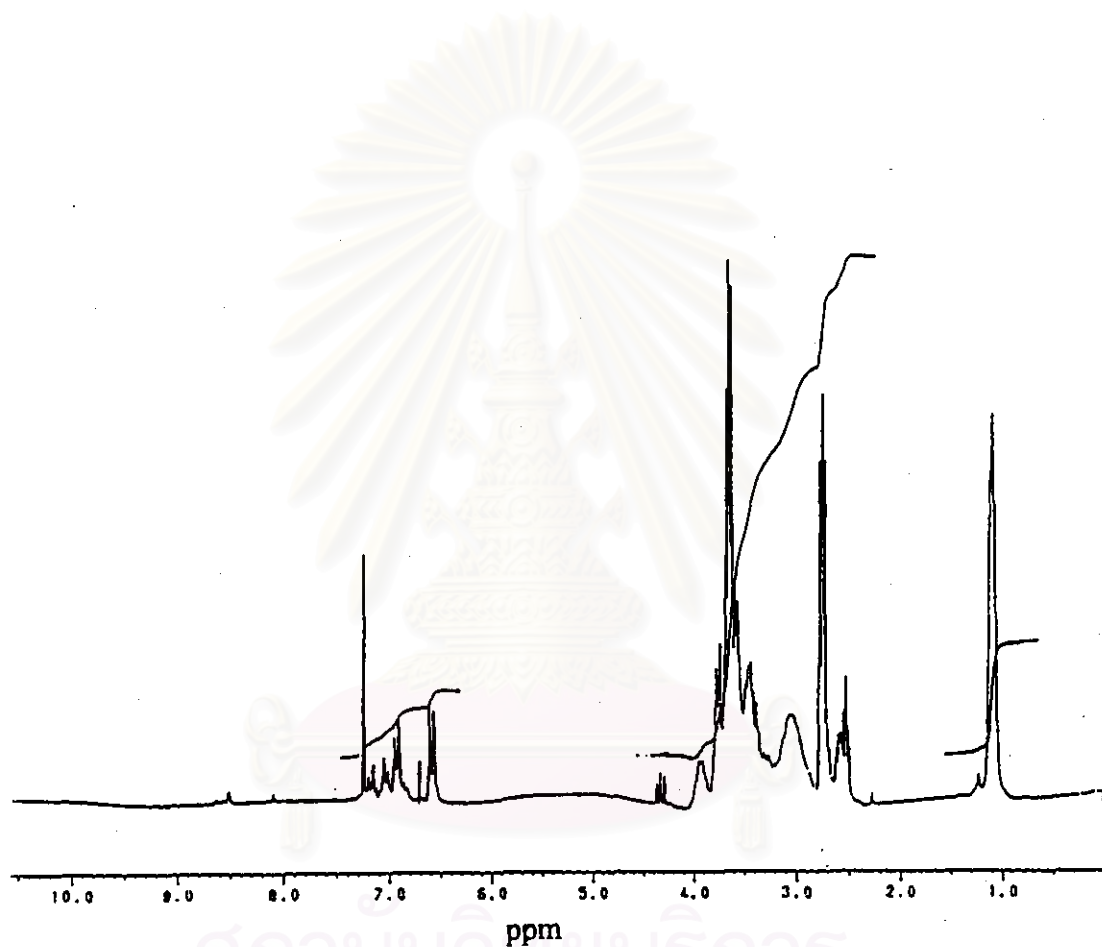**Figure 4.9** ¹H NMR spectrum of GP11

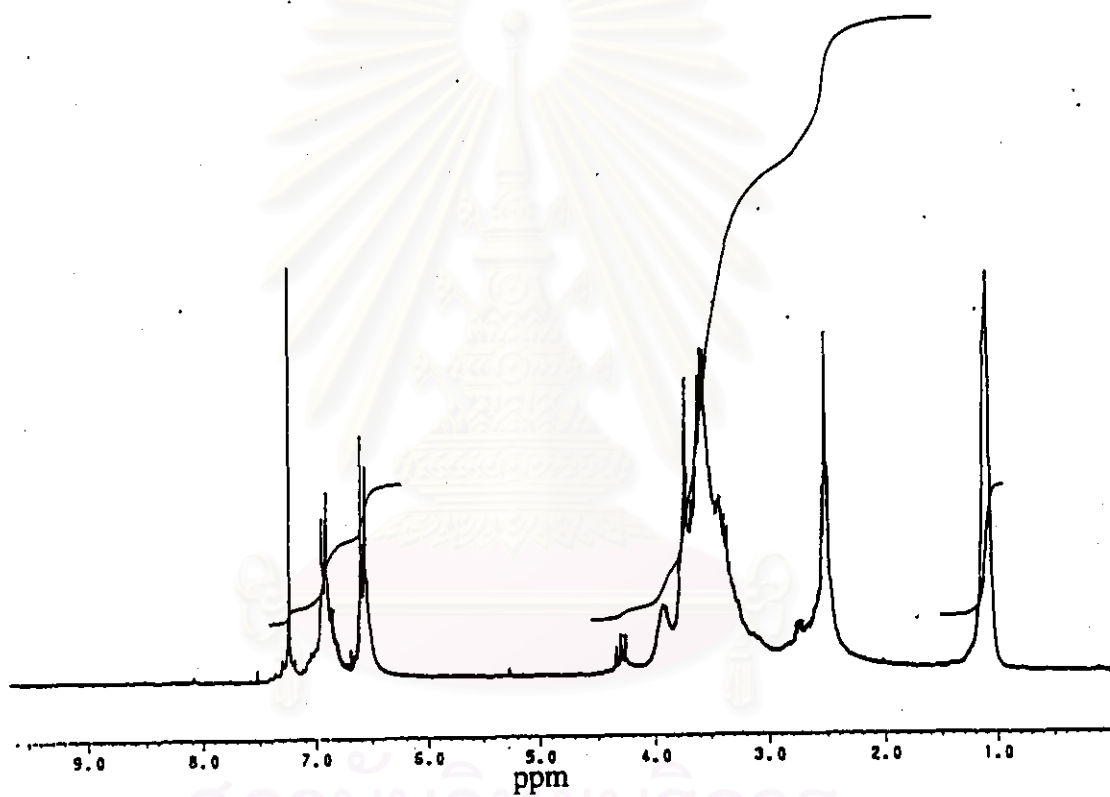**Figure 4.10** ¹H NMR spectrum of GP31

According to Figures 4.9 and 4.10, it can be determined that peaks at around 7.05 ppm and 7.20 ppm are generated from protons on aromatic rings adjacent to urethane groups as shown in Figure 4.11.
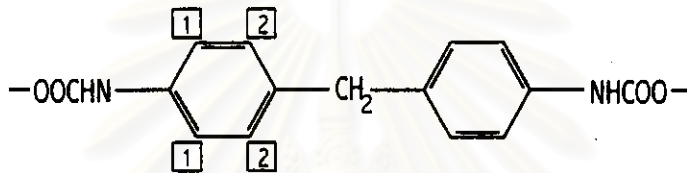

Figure 4.11 Chemical structure of a segment in polyurethane foam
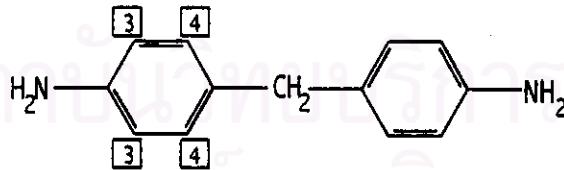

Figure 4.12 Chemical structure of methylene diphenyl amine

Peaks at around 6.60 ppm and 6.95 ppm are resulted from protons on aromatic ring next to amine groups as shown in Figure 4.12

From the aromatic proton signals in Figure 4.9, mainly two types of aromatic molecules were found. The peaks at 7.05 ppm and 7.20 ppm in the spectrum of GP11 indicate a small amount of the remaining urethane groups in the glycolyzed product. The peaks at 6.60 ppm and 6.95 ppm indicate the generation of a new substance which is probably methylene diphenyl amine. In addition, peaks at 3.7 ppm and 2.7 ppm indicate a large amount of diethanolamine remaining in the glycolyzed product, GP11.

In spectrum of GP31, there is no significant peaks at 7.05 ppm and 7.20 ppm. It is clear that almost all urethane groups disappear after the decomposition. Large peaks at 6.60 ppm and 6.95 ppm show the generation of a large amount of methylene diphenyl amine. Moreover, there is only a small amount of diethanolamine still remains in the glycolyzed product as indicated by the small peak at 2.7 ppm.

Glycolyzed products were also characterized by ^{13}C NMR spectroscopy. Figure 4.13 and Figure 4.14 show the ^{13}C NMR spectra of GP11 and GP 21. ^{13}C NMR spectrum of GP31 is similar to that of GP 21.
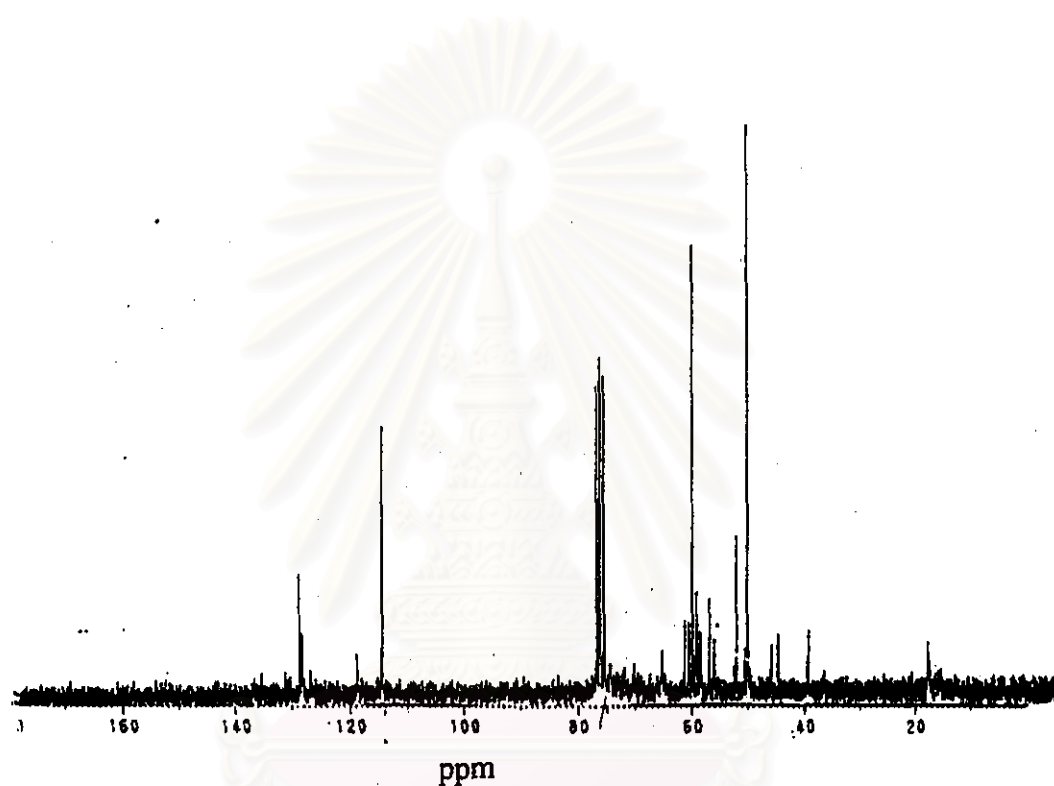
Figure 4.13 ^{13}C NMR spectrum of GP11
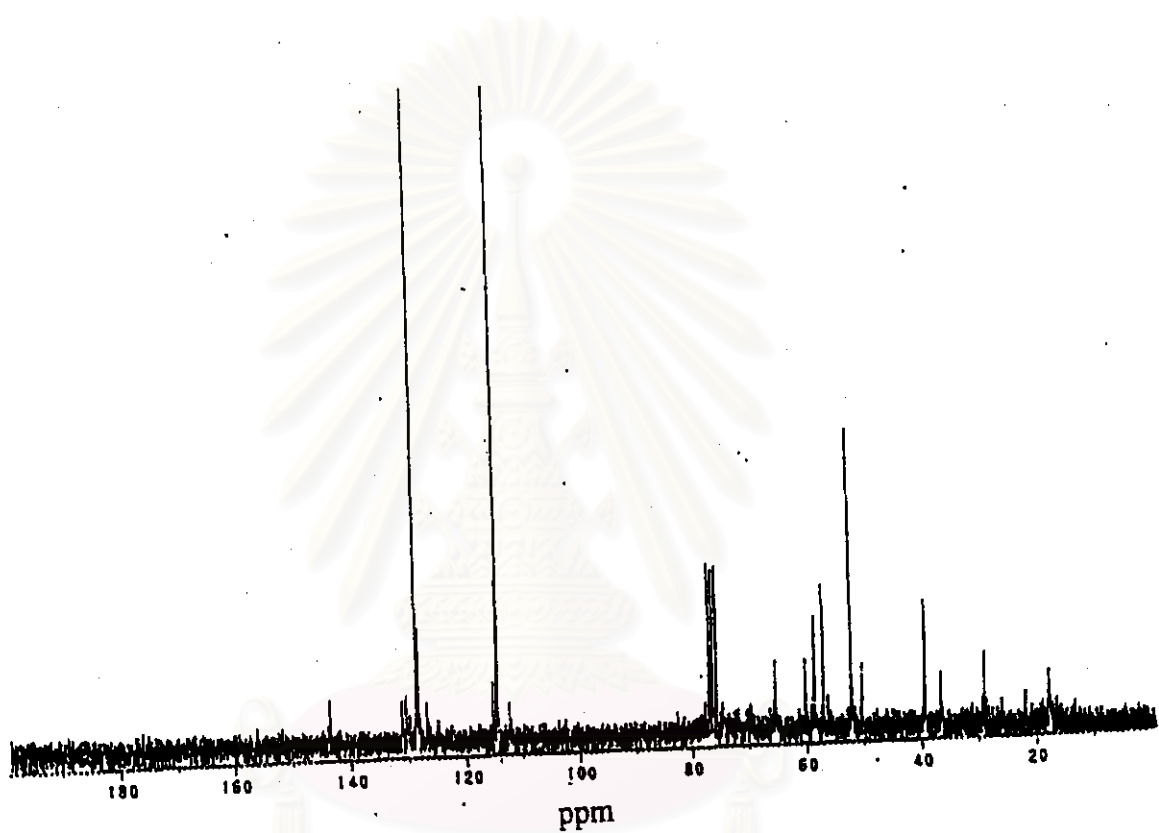
Figure 4.14 ^{13}C NMR spectrum of GP21

It is known that bands at 118.5 ppm and 128 ppm are the bands of carbon atoms on aromatic rings at the positions 2 and 1 as shown in Figure 4.11 and bands at 114.5 ppm and 129 ppm are the bands of carbon atoms on aromatic rings at the positions 4 and 3 as shown in Figure 4.12. From Figure 4.13 (GP11) low intensity bands at 118.5 ppm and 128 ppm indicate a small amount of the remaining urethane groups. The bands at 114.5 ppm and 129 ppm indicate the presence of methylene diphenyl amine. From the high intensity bands at 50.5 ppm and 60 ppm, it can be seen that a large amount of diethanolamine remains in the glycolyzed product.

According to Figure 4.14 (GP21), the bands at 118.5 ppm and 128 ppm cannot be clearly observed. It can be said that almost all urethane groups were consumed during the decomposition process. High intensity bands at 114.5 ppm and 129 ppm show the generation of a large amount of methylene diphenyl amine. In addition, the low intensity bands of diethanolamine indicate that only small amount of diethanolamine still remaining in the glycolyzed product.

Based on the IR and NMR results mentioned earlier, it can be concluded that urethane and urea groups of polyurethane foam are converted into aromatic primary amines. These results agree with the decomposition schemes shown in Figures 4.1 to 4.3. Thus, the glycolyzed products are composed of mainly aromatic primary amines, polyol, and some diethanolamine used as the decomposer.

The glycolyzed products, GP11, GP21, and GP31 were characterized by GPC using polystyrene as standards. GPC chromatograms of the glycolyzed products are shown in Figures 4.15 to 4.17. The corresponding molecular weight for each peak is shown in the Figures.
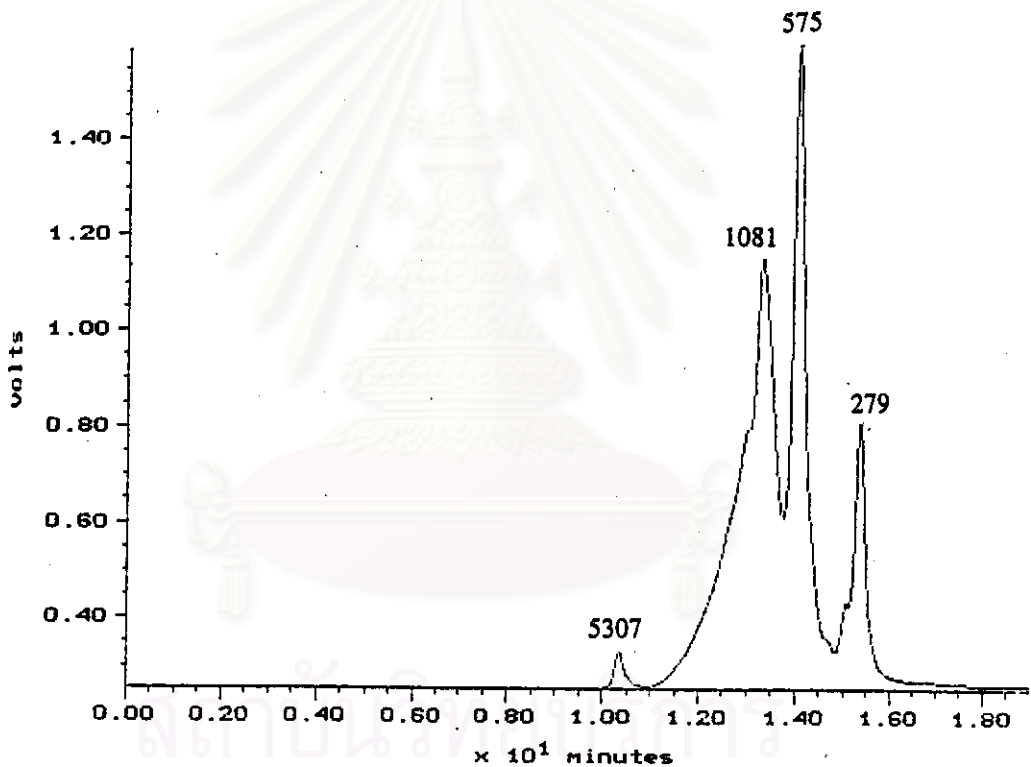

Figure 4.15 GPC chromatogram of GP 11
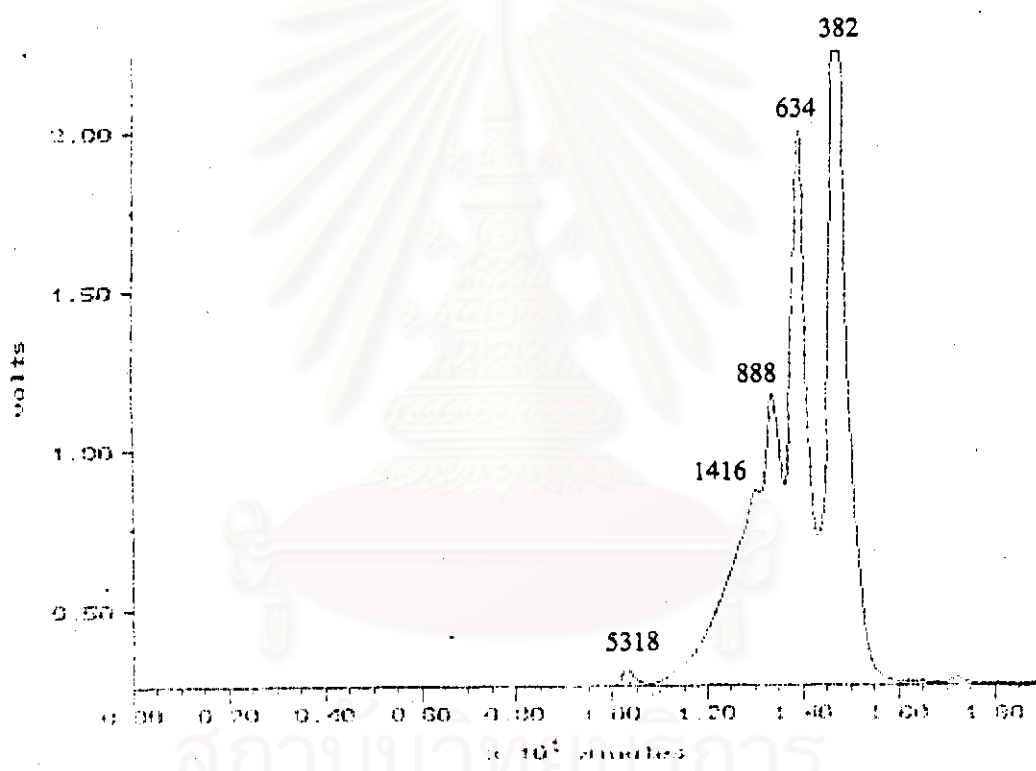
Figure 4.16 GPC chromatogram of GP 21
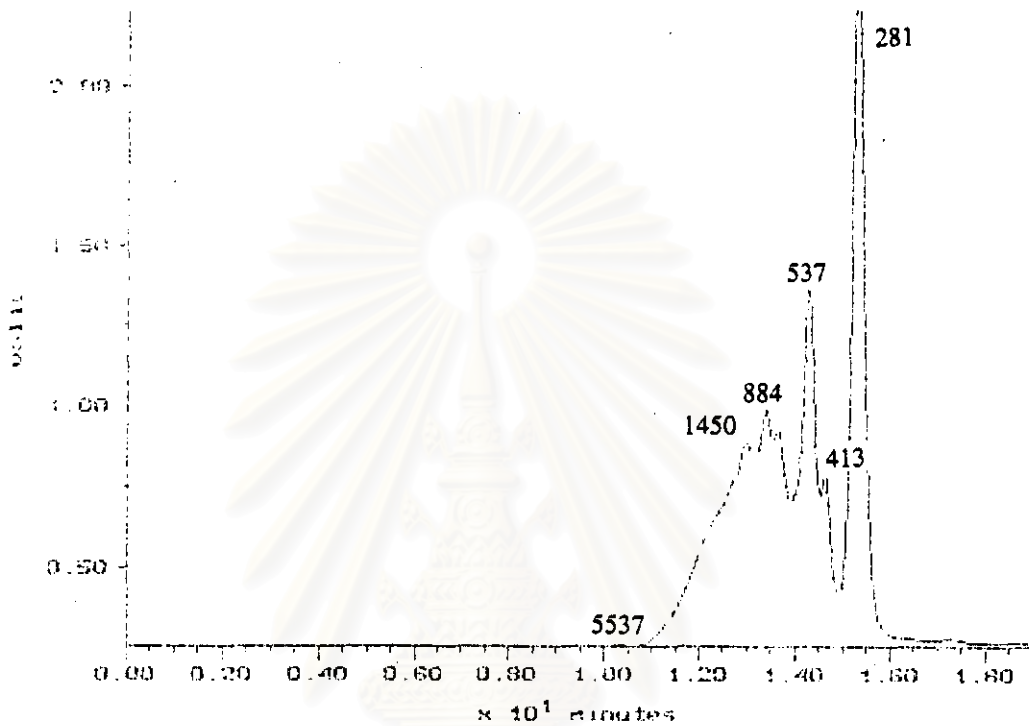
Figure 4.17 GPC chromatogram of GP 31

According to peaks in the chromatograms, many fractions of different molecular weights are found. Molecular weights of the glycolyzed products are mostly in the range of 280 to 1,100 g/mol. A shoulder peak with a molecular weight of about 1,400 g/mol was also found. In addition, each chromatogram shows a peak of significant high molecular weight of over 5,000 g/mol. This peak may be resulted from the polyol used for making the polyurethane foam. The molecular weight averages for these three glycolyzed products are summerized in Table 2.

Table 2 Molecular weight averages of the glycolyzed products

Samples	Mn (g/mole)	Mw (g/mole)
GP11	655	913
GP21	393	541
GP31	474	731

4.2 Curing of Epoxy Resin by Glycolyzed Products

All three types of the glycolyzed products contain a number of amine and hydroxyl groups. Therefore, these products can be used as a hardener for the curing of bisphenol A type epoxy resin. Samples based on a wide range of glycolyzed product to epoxy resin ratios were investigated.

Ethylenediamine was used as a model compound in order to examine the reaction of amine with epoxy resin. The reaction scan thermogram of the mixture of ethylenediamine and epoxy resin is shown in Figure 4.18. An exothermic peak was found with a peak temperature of 92 °C. The onset point of this peak was observed at 65 °C indicating that the reaction progressed dramatically at around this temperature. The peak temperature implies that the amine reacts substantially with epoxy resin. The reaction reached a completion at around 130 °C as illustrated in the reaction peak as well.
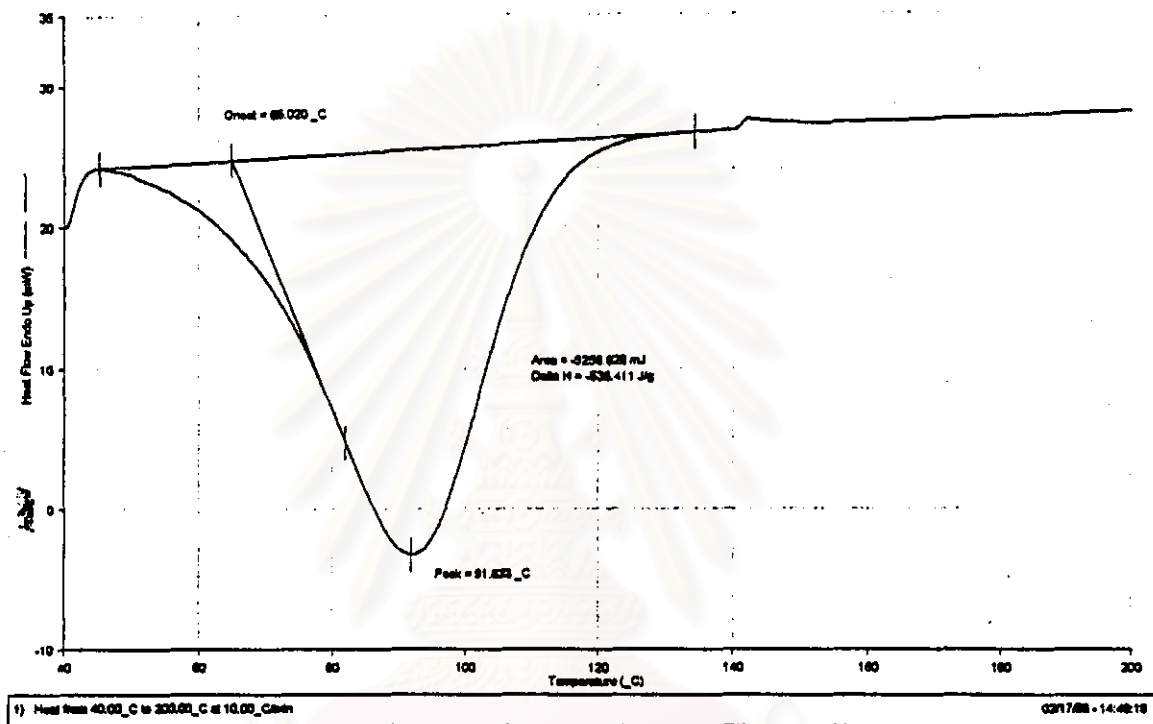
Figure 4.18 The reaction scan thermogram of the mixture of ethylenediamine and epoxy resin

Figures 4.19 to 4.21 show the reaction scan thermograms of P1112, P2111 and P3111. P1112, P2111, and P3111 refer to the GP11, GP21, and GP31 based samples respectively. The last two digits of each cured samples indicate the weight ratio of glycolyzed product to DGEBA epoxy resin. From these DSC thermograms, it can be found that the curing reactions occur substantially at temperature of approximately 120 to 150 °C determined by the exothermic peaks . The reactions can be both reactions of epoxy with amines and that of epoxy with hydroxyl groups.

Figure 4.19 Reaction scan thermogram of P1112

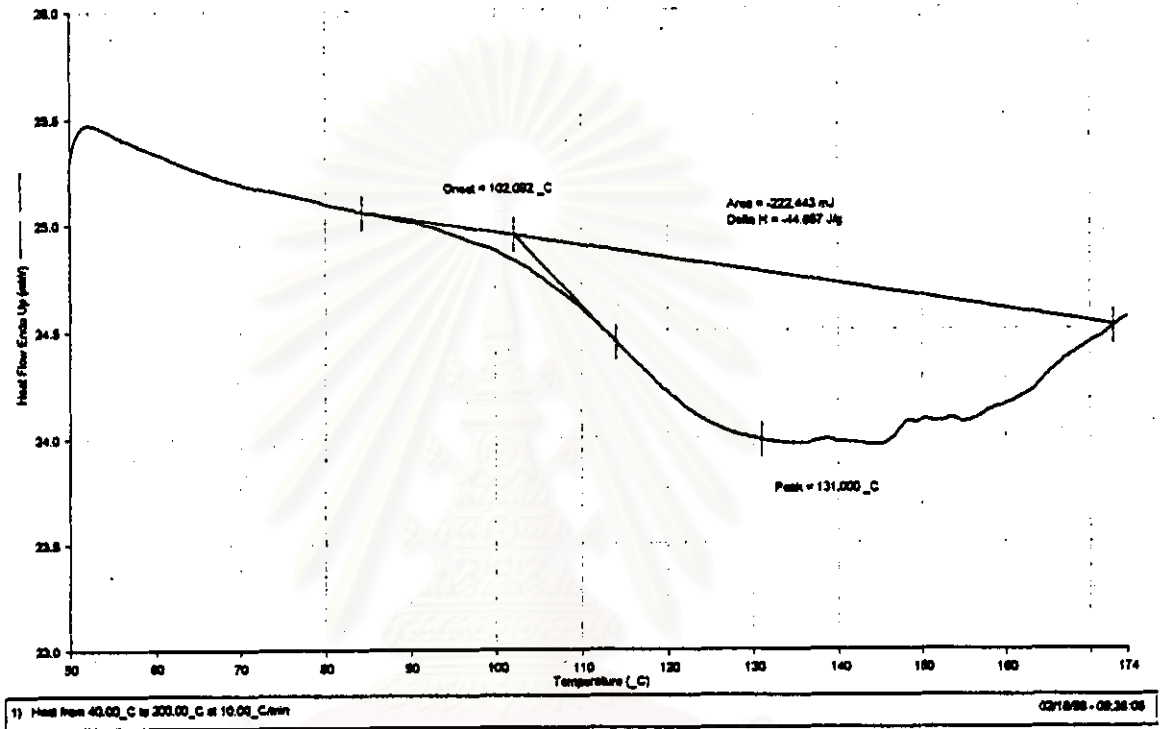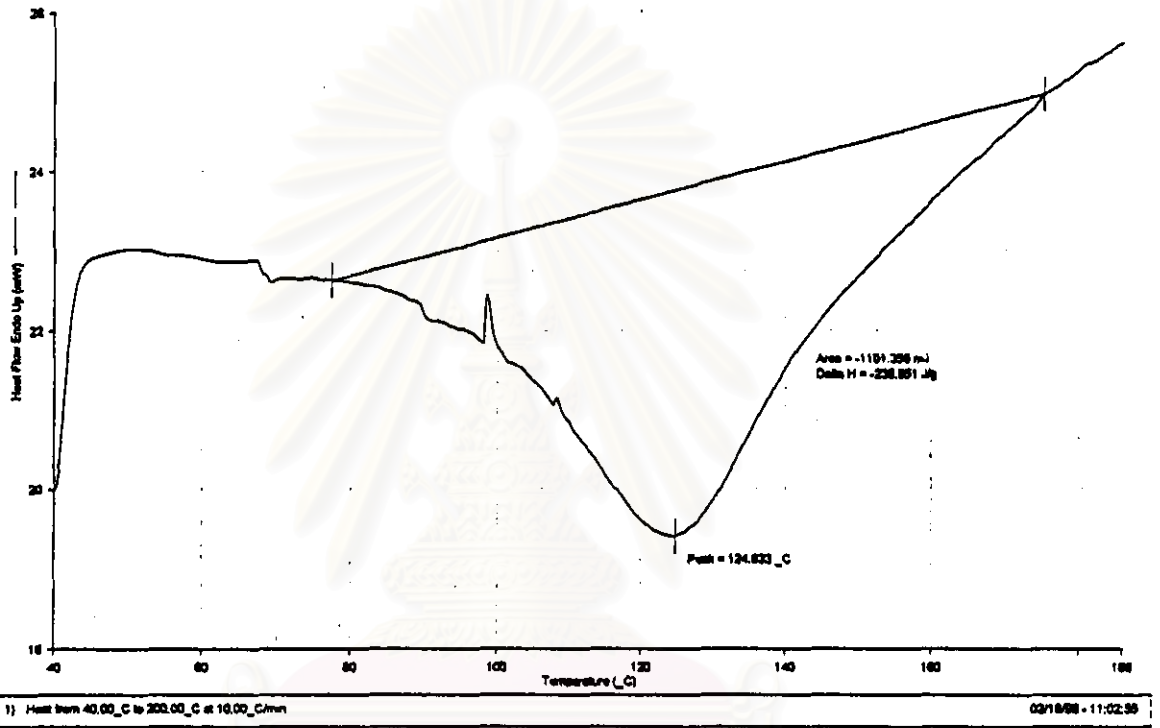**Figure** 4.20   Reaction scan thermogram of P2111
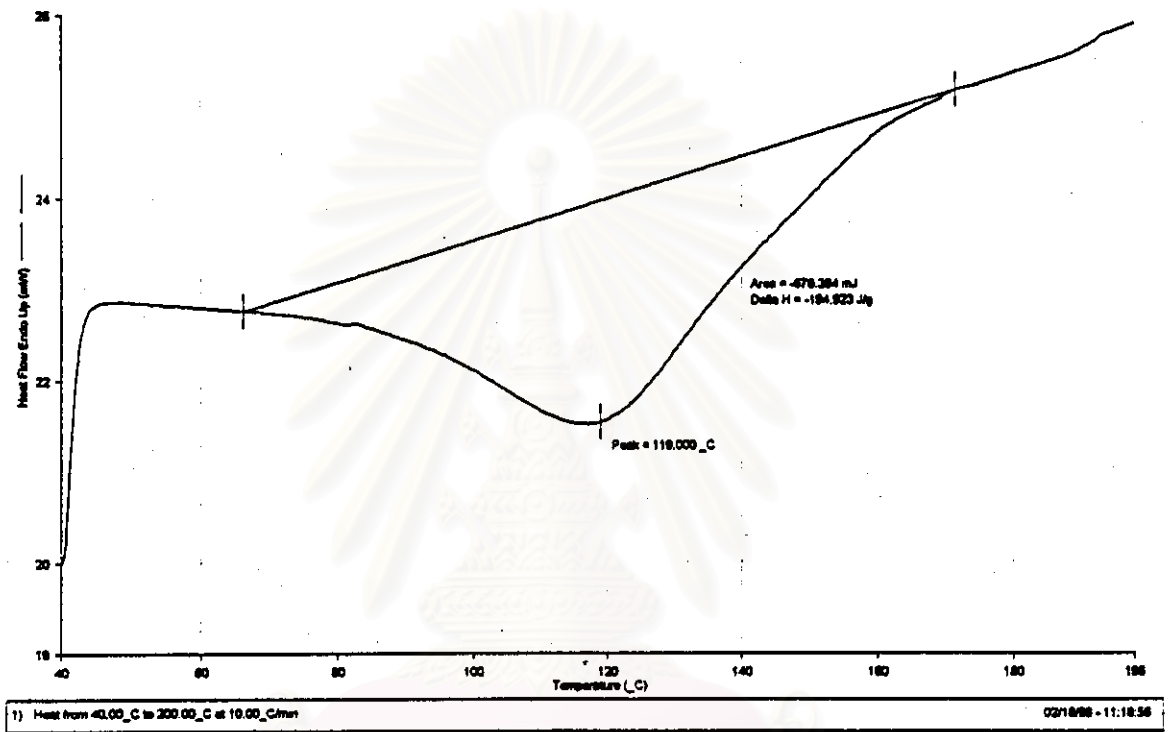
Figure 4.21 Reaction scan thermogram of P3111

According to the reaction scan thermograms shown in Figures 4.13 to 4.15, the exothermic peak is observed in every thermogram. The exothermic peaks are due to the reaction of amines and epoxy resin. The reaction of aliphatic amine with epoxy resin occurs first because it requires lower temperature than that of aromatic amine. However, the onset point of the reaction peak happens at a higher temperature than in Figure 4.12. This might be because the concentration of aliphatic amine in the glycolyzed products is lower compared with that of the pure aliphatic amine in Figure 4.12.

The exothermic peaks occurred from the reaction of aliphatic amine in glycolyzed product with epoxy resin shown in Figures 4.13 to 4.15 proceed until the point in which almost all amine are reacted. This point should be around at 130°C, as indicated by the peak in Figure 4.12.

Typically, aromatic amine reacts with epoxy resin at a higher temperature than aliphatic amine. Thus the exothermic peaks shown in Figures 4.13 to 4.15 are continued by the reaction of the aromatic amine and epoxy resin probably together with the reaction of hydroxyl compounds and epoxy resin. However, it is difficult to separate quantitatively the reaction of amines with epoxy resin and the reaction of polyols with epoxy resin.

Diethylene glycol was used as a model compound to confirm the reaction of epoxy resin and polyols in glycolyzed products. Sodium hydroxide 0.003g was dissolved in 1g (9.5×10^{-3} mole) of diethylene glycol. This mixture was then mixed with 3.61g (9.5×10^{-3} mole) of epoxy resin. After heating at 150°C for 100 minutes,

the viscosity become significantly higher. This observation can be an evidence of reaction between hydroxyl group and epoxy at this condition.

4.3 Characterization of Cured Epoxy Resin

DGEBA epoxy resin was cured by the glycolyzed products at different weight ratios. The epoxy resin was mixed with the glycolyzed products and was then cured by an oven. Every samples was cured at 150°C for 100 minutes unless specified.

Table 3 shows all cured DGEBA epoxy resins prepared in this work and their appearance after curing.

Table 3   The appearance of cured epoxy resins

GP 11 based samples		GP 21 based samples		GP 31 based samples	
Samples	Appearances	Samples	Appearances	Samples	Appearances
P 1141	Very viscous brown liquid	P 2141	Very viscous brown liquid	P 3141	Very viscous brown liquid
P 1131	Very viscous brown liquid	P 2131	Very viscous brown liquid	P 3131	Very soft brown and sticky material
P 1121	Very viscous brown liquid	P 2121	Very soft brown and sticky material	P 3121	brown solid with bubbles
P 1111	Very soft brown and sticky material	P 2111	brown solid with bubbles	P 3111	brown solid
P 1112	brown solid with bubbles	P 2112	brown solid	P 3112	brown solid
P 1113	brown solid	P 2113	brown solid	P 3113	brown solid
P 1114	brown solid	P 2114	brown solid	P 3114	brown solid
P 1115	brown solid	P 2115	brown solid	P 3115	brown solid
P 1116	brown solid	P 2116	brown solid	P 3116	brown solid

Glass transition temperatures (T_g) of various samples prepared from GP 11 and DGEBA epoxy resin at different ratios were measured by Differential Scanning Calorimetry. All samples in Figure 4.22 except P1111 are rigid and crosslinked polymers.
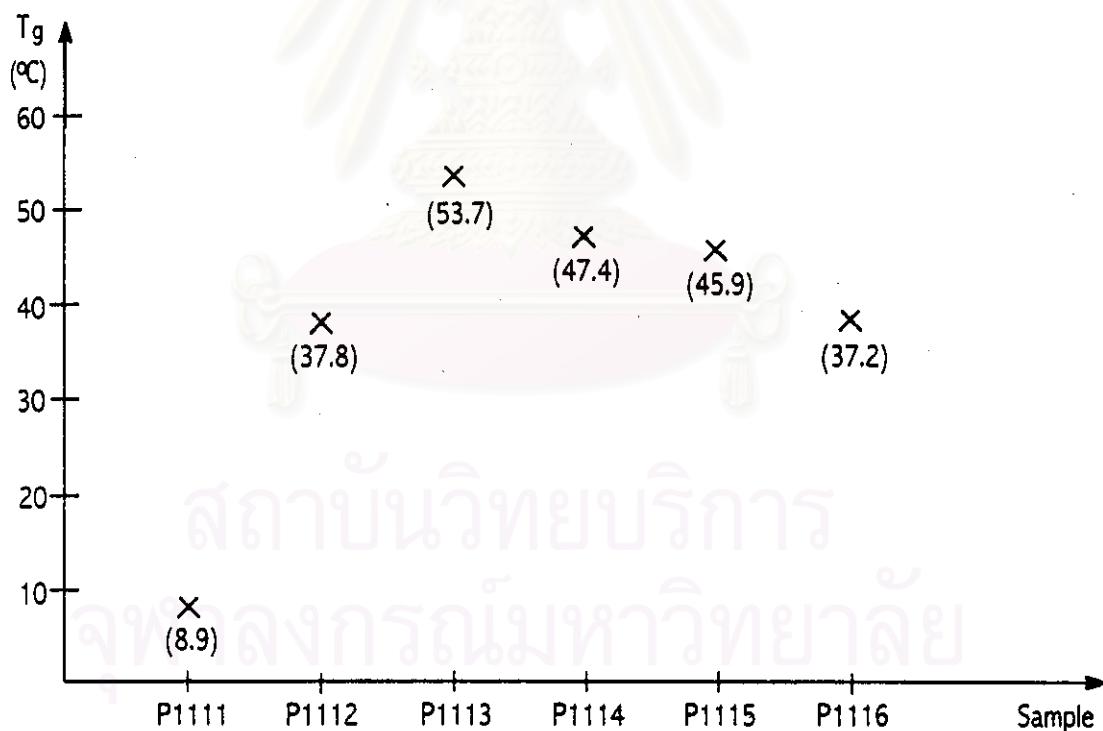

Figure 4.22 T_g of various samples based on GP 11

It is clear that T_g increases with the decreasing of ratio of the glycolyzed product to epoxy resin until a ratio of approximately 1:3. After this ratio, T_g decreases as the amount of DGEBA increases. The P1113 has the highest T_g. It might be because this ratio is close to the stoichiometric ratio of reactants. A suitable ratio of both reactants is necessary to achieve the optimization of thermal and physical properties of the materials.

Vicat softening points of such samples were measured. The results are shown in Figure 4.23.
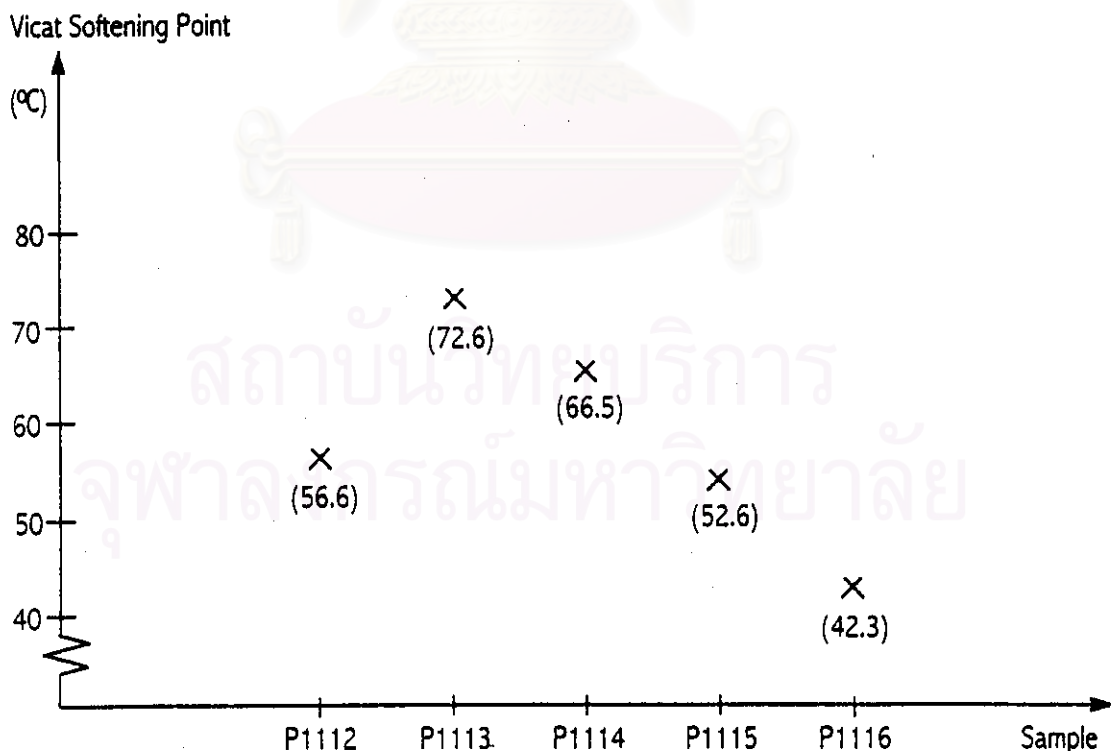

Figure 4.23   Vicat softening points of samples based on GP 11

It can be seen that Vicat softening points are above T_g of polymers for every sample. In addition, both curves possess same tendency and have the same highest point at the ratio 1 to 3 .

The DSC was also used for measuring T_g of samples based on GP21 and GP31. However, the endothermic changs of the heat capacity in thermograms are ambiguous leading to the difficulty in determining exact T_g . This problem is often seen in highly crosslinked samples. Therefore, T_g of samples based on GP 21 and GP 31 was measured by Dynamic Mechanical Analysis (DMA). The DMA thermogram of sample P3114 is shown in Figure 4.24.

The sample shows a very high storage modulus, E', similar to common rigid thermosetting materials [34]. A Tg of 92.4°C was observed based on the tan δ peak. A drop in storage modulus and a corresponding loss modulus was also observed during the Tg transition.
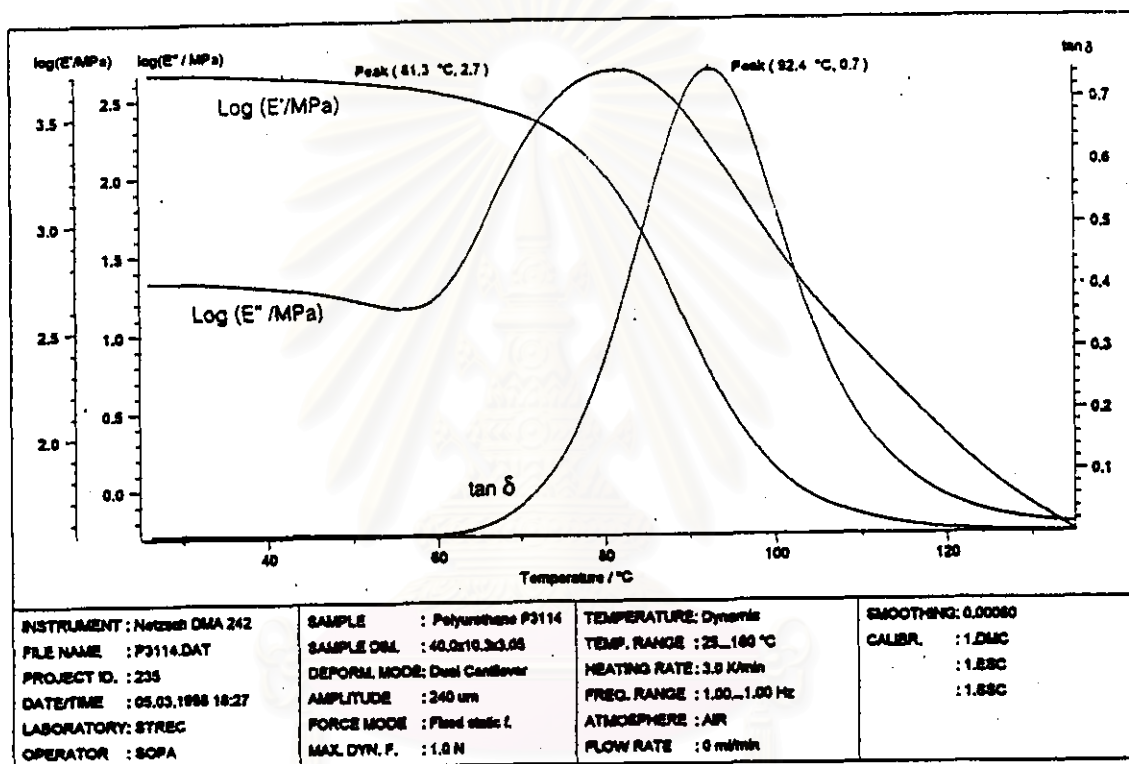
Figure 4.24 DMA thermogram of sample P3114

The T_g measured by DMA are shown in Tables 4 and 5 .

Table 4 T_g of the samples based on GP 21

Sample	T_g (°C)
P 2111	55.3
P 2112	83.6
P 2113	103.8
P 2114	105.4

Table 5 T_g of the samples based on GP 31

Sample	T_g (°C)
P 3111	61.5
P 3112	97.7
P 3113	103.8
P 3114	92.4

As shown in Tables 4 to 5, it is observed that, like the GP 11 based samples, T_g of GP 31 based samples increases with increasing of weight of DGEBA epoxy resin. However, after a weight ratio of glycolyzed product to epoxy resin at 1 to 3 which provides the highest Tg value, Tg of GP31 based samples decreases when the weight of epoxy resin increases. In the case of GP 21 based samples, it can be assumed that after increasing of T_g with increasing of the weight of epoxy resin, T_g will also decrease as the weight of epoxy resin increases. These observation can be explained by the same reason for GP 11 based samples.

Hardness of cured epoxy resin was measured by the Shore Durometer Type D unless specified.

Hardness of various samples are shown in Tables 6 to 8. All hardness measurements were carried out at ambient temperature.

Table 6   Hardness of samples based on GP11

Sample	Hardness	Average	Standard deviation
P1111	30 shore A, 35 shore A, 40 shore A, 30 shore A, 30 shore A	33.0 A	4.5
P1112	65,70,70,70,68	69.2	2.2
P1113	68,70,72,70,70	70.0	1.4
P1114	70,72,68,68,75	70.6	3.0
P1115	65,68,70,75,70	69.6	3.6
P1116	70,70,68,72,70	70.0	1.4

Table 7   Hardness of samples based on GP21

Sample	Hardness	Average	Standard deviation
P2111	65,63,65,68,65	65.2	1.8
P2112	70,75,70,70,68	70.6	2.6
P2113	75,75,70,72,70	72.4	2.5
P2114	75,72,70,70,68	70.9	2.6
P2115	75,75,75,70,70	73.0	2.7
P2116	70,70,70,70,68	69.6	0.9

Table 8   Hardness of samples based on GP31

Sample	Hardness	Average	Standard deviation
P3111	68,75,70,68,70	70.2	2.9
P3112	72,72,72,70,68	70.8	1.8
P3113	75,75,75,75,75	75.0	0.0
P3114	75,75,70,70,70	72.0	2.7
P3115	70,70,75,72,70	71.4	2.2
P3116	70,70,70,70,72	70.4	0.9

From these Tables, it is shown that there is no significant difference in the hardness values of every sample at the temperature of above T_g of such samples. All hardness values of rigid samples are in a range of 65 to 75 D. These values are similar to that of polypropylene.

The resin was cured in a polystyrene petri dish. The sample was then placed on top of the picture. Figure 4.25 shows the appearance, color and clarity of sample P3114.

Figure 4.25 Appearance of sample P 3114

Figure 4.26 shows the modified sample P3114. Pigment was dispersed in the sample and the sample was then precured at an ambient temperature. When the resin became rubbery, it was shaped into a desired configuration. The preparation of this sample demonstrated that the polymer resins possess good processibility and can potentially be used in variety of applications.

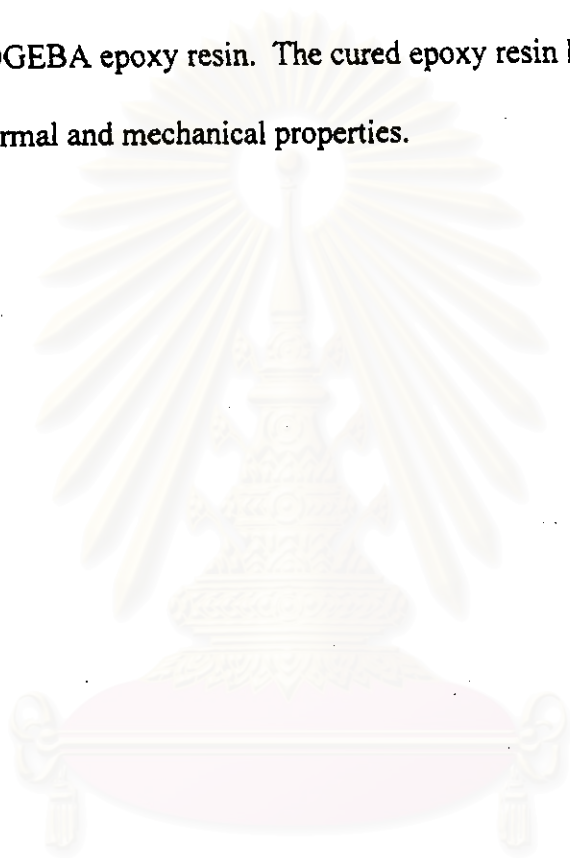Figure 4.26   A sample made of pigmented P 3114

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Good processibility is found in DGEBA epoxy resin cured with the glycolyzed products. This resin can be precured and shaped into a desired configuration.

This work demonstrates that rigid polyurethane foam can be efficiently recycled by glycolysis method. The glycolyzed products obtained can be used as a curing agent of DGEBA epoxy resin. The cured epoxy resin has good appearance and exhibits good thermal and mechanical properties.