

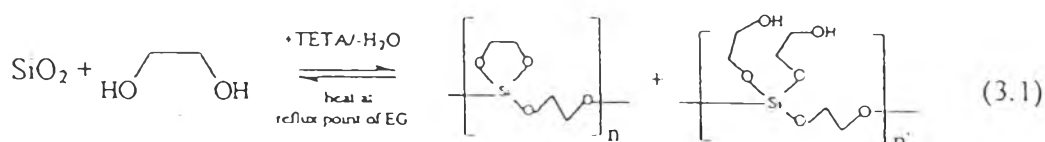
## CHAPTER III

### RESULTS AND DISCUSSION

#### 3.1 Synthesis

##### 3.1.1 Synthesis of Glycolato Siloxane Polymer

In this study, glycolato siloxane polymer products were synthesized from silicon dioxide, SiO<sub>2</sub>, and ethylene glycol, EG, in the presence of triethylenetetramine, TETA, as a base. Because water is a by-product of the reaction, it must be removed from the system to drive the reaction forward and prevent gelation, as shown in equation (3.1):



In this system, the reaction mixture started as a two phase mixture composed of SiO<sub>2</sub>, ethylene glycol and TETA. When the reaction was achieved, the mixture homogeneously turned clear. The product was purified by precipitating in 2.5% dried MeOH in dried CH<sub>3</sub>CN. A slight amount of MeOH helped to precipitation.

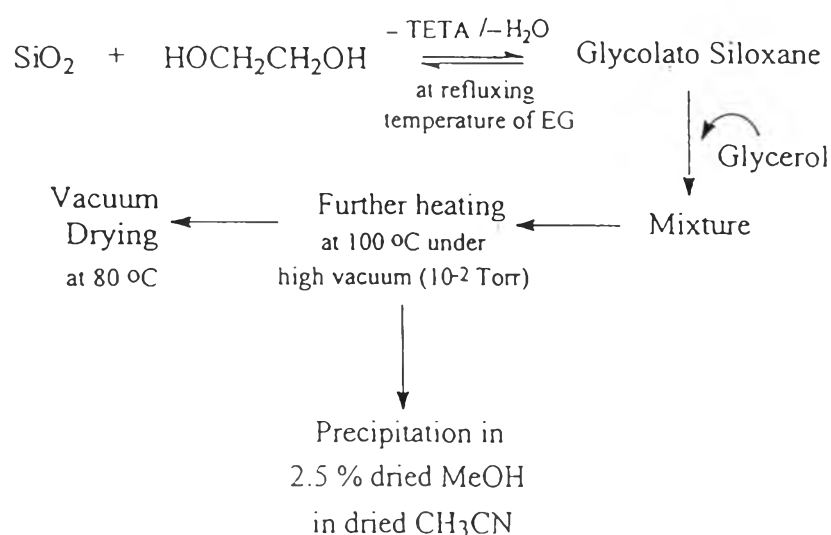
##### *Effect of TETA Concentration on Glycolato Siloxane Polymer*

The study was conducted at TETA concentration of 10 mol% (25 mmol, 100 mmol of N equivalent), 15 mol% (37.5 mmol, 150 mmol of N equivalent), 20 mol% (50 mmol, 200 mmol of N equivalent), 25 mol% (62.5 mmol, 250 mmol of N equivalent), and 30 mol% of SiO<sub>2</sub> (75 mmol, 300 mmol of N equivalent), respectively. The mixture reaction took 25 h. to complete,

and at this point the mixtures were clear when they were allowed to cool down, indicating that the reactions were completed. Therefore, the appropriate time for Si(eg)<sub>2</sub> synthesis at each TETA concentrations was at 25 h.

### 3.1.2 Crosslinking Step with Glycerol

*Addition of Glycerol to Glycolato Siloxane Polymer (Scheme VII)*



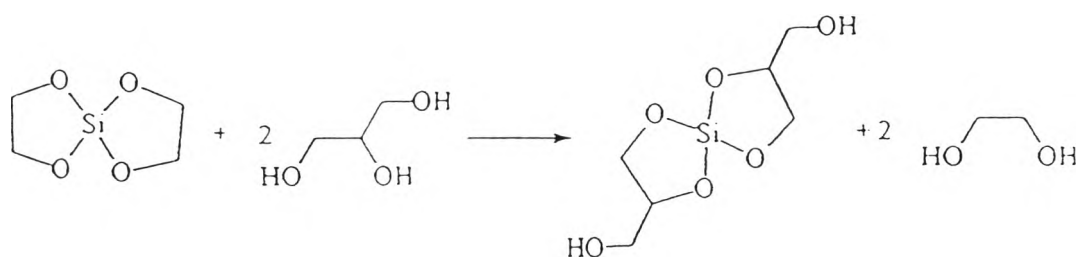
**Scheme VII : Crosslinking glycolato siloxane polymer with glycerol.**

The synthesis results were acquired, based on Scheme VII reaction route. The TGA data (see Table 3.1) will be discussed along with other results.

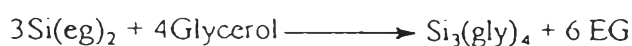
Table 3.1 : Percent Ceramic yields of crosslinking products at different TETA concentration and different crosslinking reaction times

TETA Conc. Crosslinking time	15 mol%	20 mol%	25 mol%	30 mol%	100 mol%
	10 hr	42.1	51.2	53.6	40.1
15 hr	46.8	42.4	53.9	40.5	-
20 hr	43.5	65.8	41.5	51.3	-
40 hr	-	-	-	-	43.7
50 hr	-	-	-	-	7.6

The mixture was further heated at 100°C under high vacuum ( $10^{-2}$  Torr), to eliminate remaining EG. Meanwhile the exchange reaction between EG and glycerol occurred, as illustrated below (Scheme VIII).



Theoretical percent ceramic yield = 28.9



Theoretical percent ceramic yield = 40.9

### Scheme VIII : Exchange reaction between EG and glycerol.

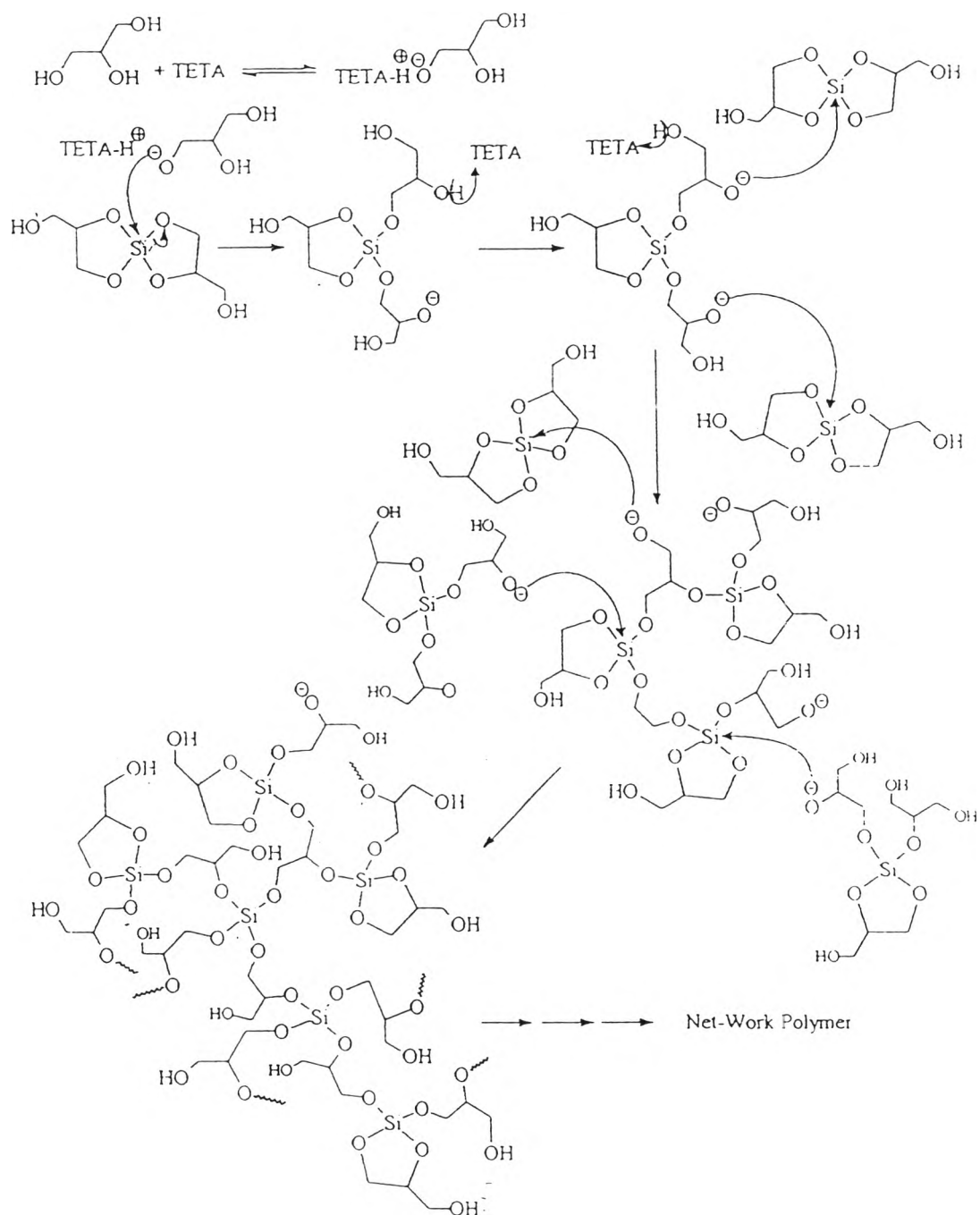
The obtained product gave a TGA profile with a relatively high % ceramic yield as compared to  $\text{Si}(\text{gly})_2$  which has theoretical ceramic yield of 28.9%. This suggests that the product might be crosslinked, see Scheme IX, since the system had excess glycerol and was run in the presence of TETA.

#### 3.1.3 Effect of TETA Concentration on Crosslinked Polymer Product

The synthesis of glycolato siloxane polymer was first carried out in  $\text{N}_2$  atmosphere. Varied TETA concentrations were added, and variation of the crosslinking reaction time was then studied. The crosslinking reaction was conducted under vacuum ( $\sim 10^{-2}$  Torr) at  $100^\circ\text{C}$ .

From Table 3.1, the range of ceramic yields was approximately from 40 to 60 % except when excess TETA concentration was applied. At 50 h. of crosslinking time, percent ceramic yield dropped dramatically. The reason for this is in the later section.

The effect of TETA concentration on the formation of network structure is considered simultaneously with the effect of crosslinking time.



**Scheme IX : Synthesis of glycolato siloxane polymer.**

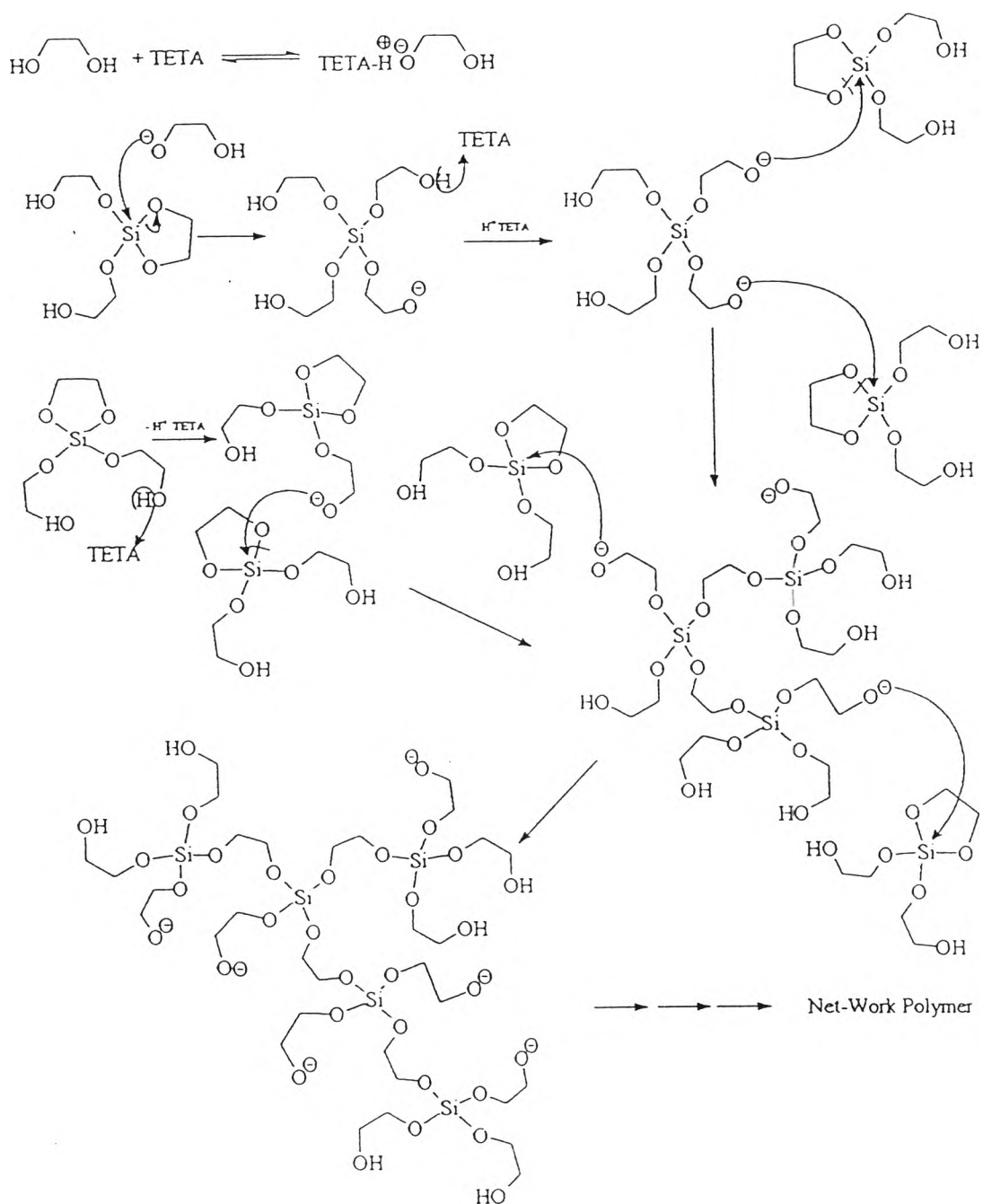
Before the crosslinking step, ethylene glycol (EG) reacted with  $\text{SiO}_2$  in the presence of TETA, as a base to form  $\text{Si}(\text{eg})_2$ . The mechanism of this reaction is shown in Scheme X. After glycerol was added in the mixture and then further heated at  $100^\circ\text{C}$  under high vacuum ( $10^{-2}$  Torr) to eliminate EG, glycerol exchanged with EG groups in  $\text{Si}(\text{eg})_2$  to give  $\text{Si}(\text{gly})_2$ . Continued reaction caused the  $\text{Si}(\text{gly})_2$  to crosslink with itself to form a network polymer, see Scheme IX. Therefore the ceramic yields after the crosslinking step should be less than those before adding glycerol since the ratio of  $\text{SiO}_2$  to organic ligands of  $\text{Si}(\text{gly})_2$  is less than that of  $\text{SiO}_2$  to  $\text{Si}(\text{eg})_2$ .

#### 3.1.4 Effect of Crosslinking Time on Crosslinked Polymer Product

From TGA data (Table 3.1), for TETA concentration of 15 mol%, the % ceramic yield did not change significantly on changing reaction time from 10 to 20 h. At 10 h. of crosslinking time, the obtained ceramic yield was 42.1 (theoretical % ceramic yields of  $\text{Si}(\text{eg})_2 = 40.5$ ,  $\text{Si}(\text{gly})_2 = 28.9$ ,  $\text{Si}_3(\text{gly})_4 = 40.9$ , and  $\text{Si}(\text{eg})(\text{gly}) = 33.7$ ). This can suggest that there might be some water left in the product which hydrolyzed some EG and glycerol groups in the polymer molecules and formed Si-O-Si bonds. These bonds caused the obtained ceramic yield to be little higher than the theoretical ceramic yield.

At 15 h. of crosslinking reaction time, the % ceramic yield increased which was the result of further hydrolysis. Even though the exchange reaction between some glycerol and EG ligands also occurred at the same time, the amount of glycerol that exchanged was less than that of hydrolysis, so the ceramic yield still increased. After 20 h. of crosslinking time, the ceramic yield decreased because more glycerol exchanged with EG groups in  $\text{Si}(\text{eg})_2$  molecules to give more crosslinked polymers.

For TETA concentration of 20 mol%, at 10 h. of crosslinking time again there was some water left in the product which caused the ceramic yield



**Scheme X : Synthesis of crosslinked glycolato siloxane polymer.**

to be higher than the theoretical ceramic yield of the crosslinked products because of the presence of Si-O-Si bonds in polymer molecules. When the reaction continued until 15 h., the exchange reaction between some EG ligands and glycerol took place, resulting in a decrease of the ceramic yield. After 20 h., the ceramic yield increased again. It might indicate that in the presence of TETA some glycerol linkages may be broken from the network and form acrolein molecules which have boiling point only 53°C and evaporated away as shown in Scheme XI.

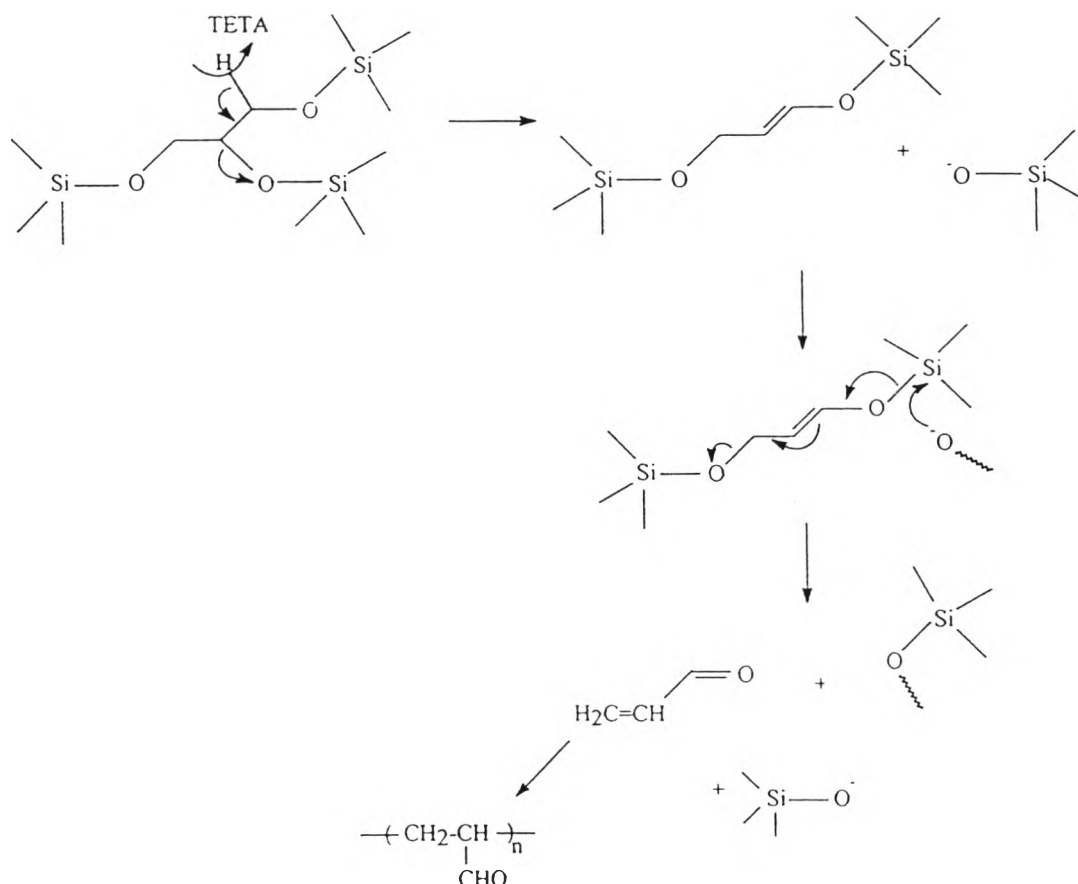
For TETA concentration of 25 mol%, 10 and 15 h. of crosslinking time gave similar network structure since the ceramic yields were slightly different. At 10 h. of crosslinking time, some Si-O-Si bonds resulted from hydrolysis of glycolato siloxane polymer caused the ceramic yield to be higher than the theoretical ceramic yield. When the reaction was conducted until 15 h., the ceramic yield increased slightly because of the further hydrolysis. As discussed previously, the exchange reaction between some glycerol and EG groups could occur at the same time, but the exchange was still less. After 20 h. of crosslinking reaction time, the ceramic yield decreased because more glycerol exchanged with EG ligands in glycolato siloxane polymers to give more crosslinked products.

With higher TETA concentration, 30 mol%, 10 h. and 15 h. of crosslinking reaction time gave the lowest ceramic yields as compared to others. This phenomenon might indicate that glycerol readily exchanged with EG ligands to form network. However, if the reaction was further conducted until 20 h. the ceramic yield increased, indicating that the network polymer broke and formed some acrolein molecules.

By using excess TETA concentration, and considering ceramic yields from Table 3.1, it is found that at 50 h. of crosslinking reaction time ceramic yield dropped dramatically. This might be because most of network



polymer underwent dehydration to give acrolein species which was then polymerized to give polymer containing no silicon in the molecule.



**Scheme XI : Formation of acrolein molecule.**

### 3.1.5 Effect of Dioctyl Phthalate on Crosslinked Polymer Product

In this step, dioctyl phthalate used as a plasticizer for softening polymer was added into glycolato siloxane polymer at 0.2, 0.3, 0.4 and 0.5 mol% of  $\text{SiO}_2$ , respectively, at the same time as the addition of glycerol before the crosslinking step. The resulting mixtures were cast as films in the vacuum oven at  $80^\circ\text{C}$  since the crosslinked films without dioctyl phthalate were extremely brittle and broken during the drying process. Dioctyl phthalate

would separate the polymer chains from each other and hence made them move easier.

The films with dioctyl phthalate concentration of 0.2, 0.3 and 0.4 mol% were still brittle and broken during the drying process. However, the crosslinked polymer containing dioctyl phthalate concentration of 0.5 mol% could be cast as films during the drying process. This means that dioctyl phthalate concentration of 0.5 mol% is a suitable concentration for casting crosslinked polymer films.

### 3.1.6 Mechanical Property, Modulus, of Crosslinked Product

The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) were measured by rheometer from 25-250°C. As shown in Figures 1-6, at low temperatures, there were usually several secondary transitions involving comparatively small changes in modulus. The polymer behaves like a hard and brittle glassy material. This is called glassy region. In this region, thermal energy is insufficient to overcome the potential barriers for rotational and translational motions of the polymer molecule segments. With increasing temperature, the amplitude of vibrational motion becomes greater, and eventually the thermal energy becomes roughly comparable to the potential energy barriers of segment rotation and translation. In this temperature region, the polymer exhibits at the glass transition temperature which was in the range of 170-200°C, at which short-range diffusional motions begin. This phenomenon was accompanied by a catastrophic decrease in the modulus. The transition region was broad because this polymer was crosslinked polymer. At temperatures over 200°C, the polymer would decompose and become brittle so the modulus increased again. Thus, we could not observe the rubbery plateau region in this crosslinked polymer.

By considering TGA data (Table 3.1) along with the modulus results, for TETA concentration of 15 mol% synthesis, the modulus of the crosslinked products did not change significantly on changing reaction time from 10 to 20 h. which corresponds to the ceramic yields that did not change much either. At 10 h. of crosslinking reaction time (Figure 1), the product gave the highest modulus compared to the other crosslinking times at the same concentration (Figure 3 and 5) meaning that at this time the polymer had the highest stiffness. The obtained ceramic yields were slightly higher than the theoretical ceramic yields because of the presence of Si-O-Si bonds in the polymer molecules. Therefore, the modulus could be less than that of polymers with less Si-O-Si bonds since Si-O-Si bonds made the polymer molecules more flexible than Si-O-C bonds.

For TETA concentrations of 20 mol%, at 10 h. of crosslinking reaction time, because of some water in the product which hydrolyzed EG and glycerol ligands in polymer chain, the ceramic yield was thus higher than the theoretical ceramic yield, resulting in a lower modulus. 15 h. of crosslinking time which gave the lowest ceramic yield compared to other crosslinking times showed the highest modulus since more glycerol exchanged with EG groups in glycolato siloxane polymer to give crosslinked product. The crosslinked product had higher modulus so it showed higher stiffness. After the reaction was continued until 20 h., the ceramic yield decreased because some glycerol linkages broke from the polymer network and formed acrolein molecules which have low boiling point and evaporated away. The modulus of polymer therefore decreased. meaning that stiffness decreased as well.

For TETA concentration of 25 mol%, 10 and 15 h. of crosslinking reaction times gave similar network structure since the ceramic yield were slightly different. Some Si-O-Si bonds resulted from hydrolysis of glycolato siloxane polymer caused the ceramic yield to be higher than the theoretical %

ceramic yield. The moduli of products obtained were thus low. The reason is as described above. 20 h. of crosslinking reaction time gave the lower ceramic yield because of the exchange reaction between some EG groups and glycerol, so it gave higher modulus, indicating the higher stiffness as well.

For TETA concentration of 30 mol%, 10 h. of crosslinking reaction time gave the highest modulus and highest stiffness since the exchange reaction between EG ligands and glycerol occurred mostly. The ceramic yield was the lowest at this condition. At 20 h. of crosslinking reaction time, the modulus decreased while the ceramic yield increased because the network polymer broke and formed acrolein molecules, as described previously.

Therefore, these results suggest that the optimum condition for crosslinked glycolato siloxane polymer is at 30 mol% of TETA with the crosslinking time of 10 h. since it gave the lowest ceramic yield. This indicates the effective of glycerol as a crosslinking reagent on exchanging with EG ligands in polymer molecules to form crosslinked network polymer.

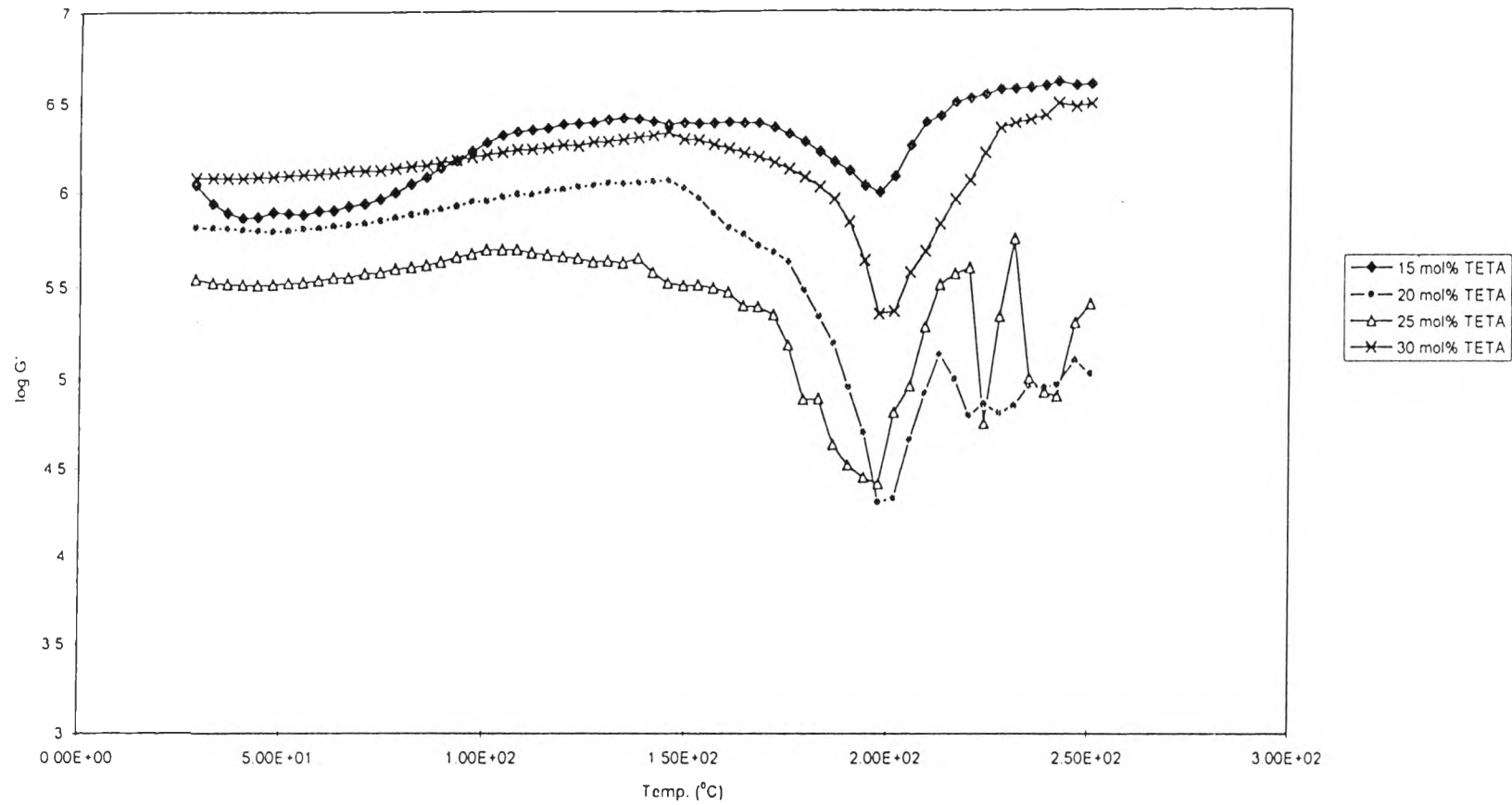


Figure 1 : Storage modulus ( $G'$ ) vs temperature of crosslinked glycolato siloxane polymer at 10 h. of crosslinking time.

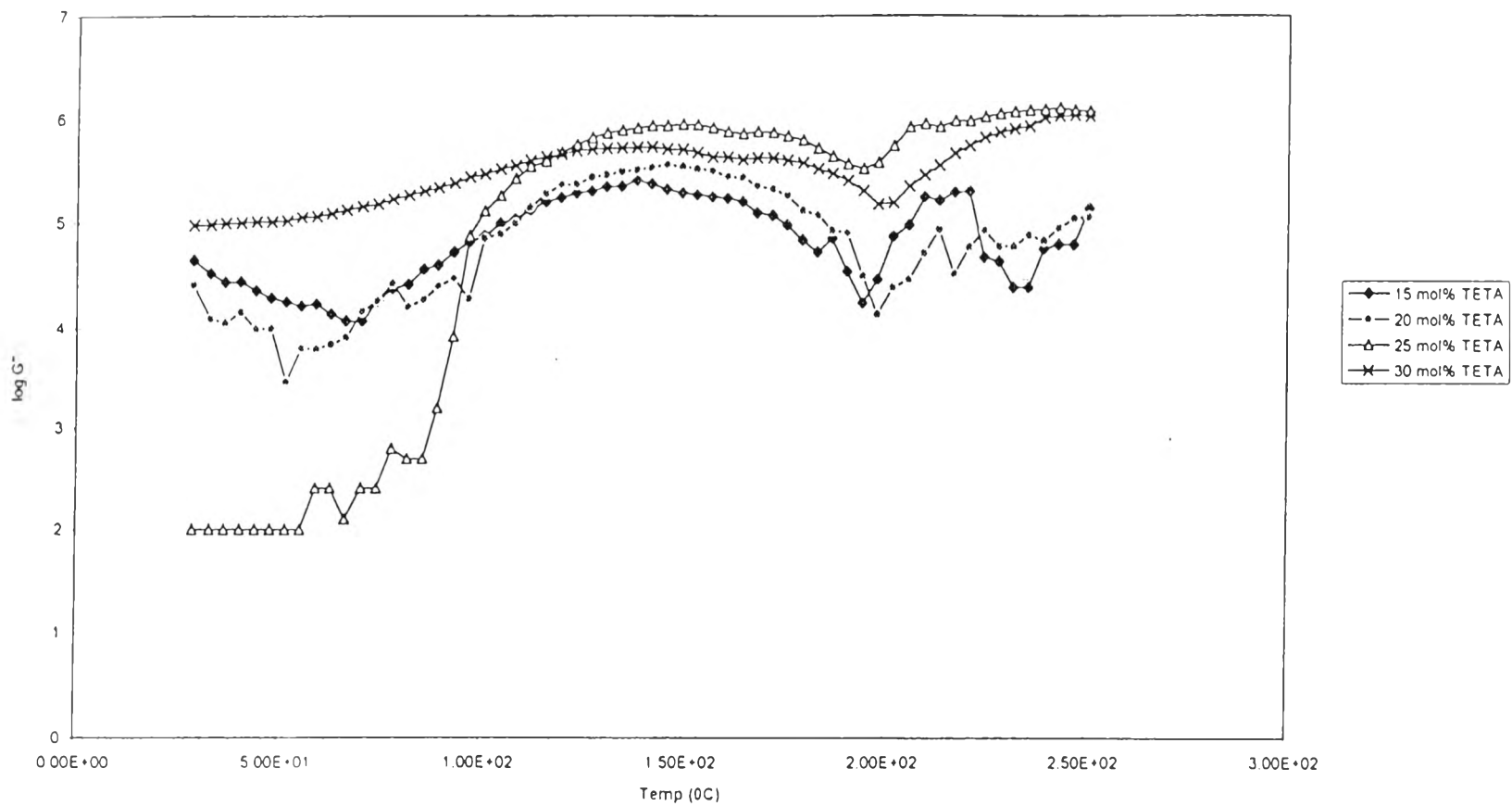


Figure 2 : Loss modulus ( $G''$ ) vs temperature of crosslinked glycolato siloxane polymer at 10 h. of crosslinking time.

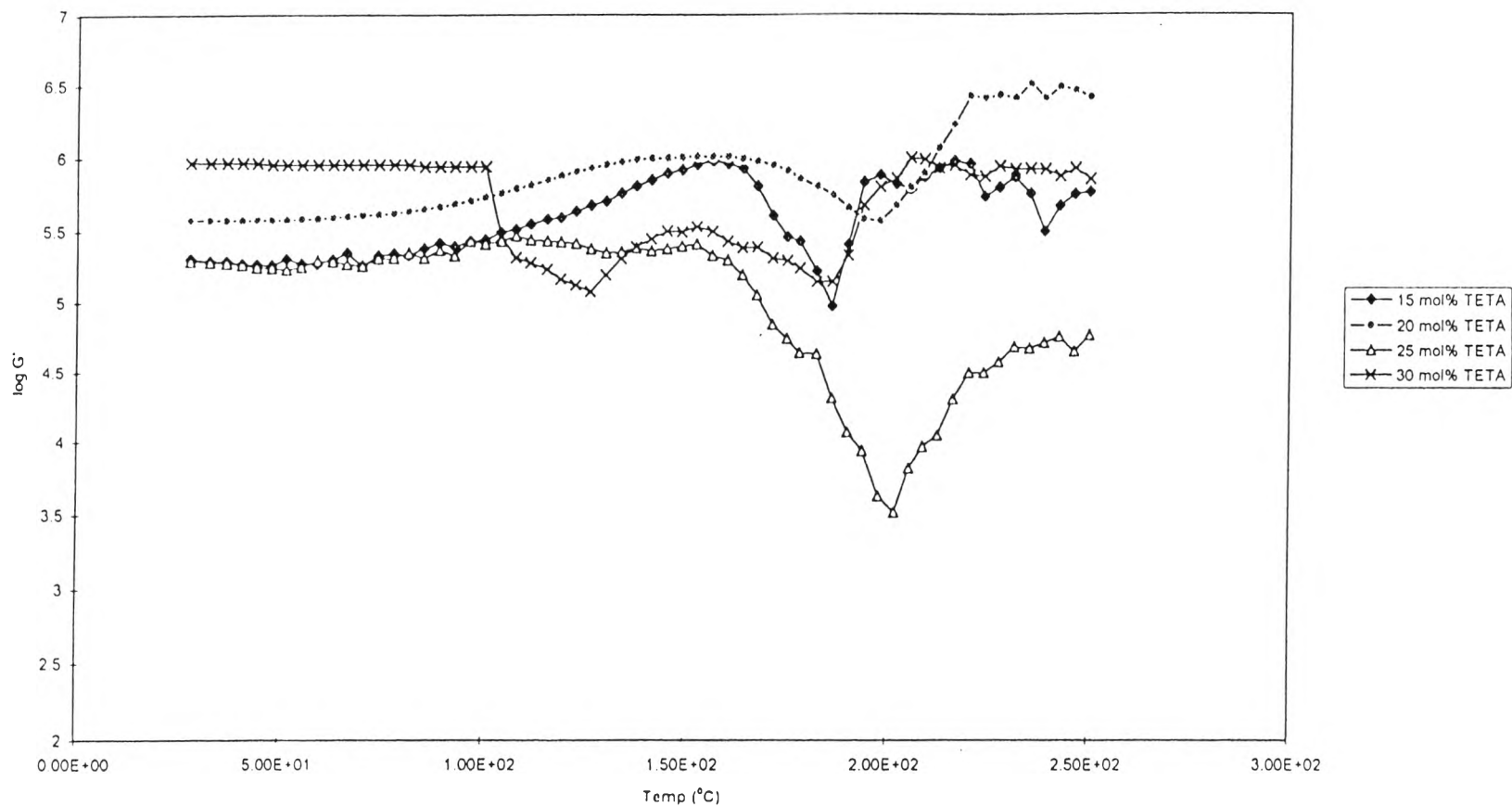


Figure 3 : Storage modulus ( $G'$ ) vs temperature of crosslinked glycolato siloxane polymer at 15 h. of crosslinking time.

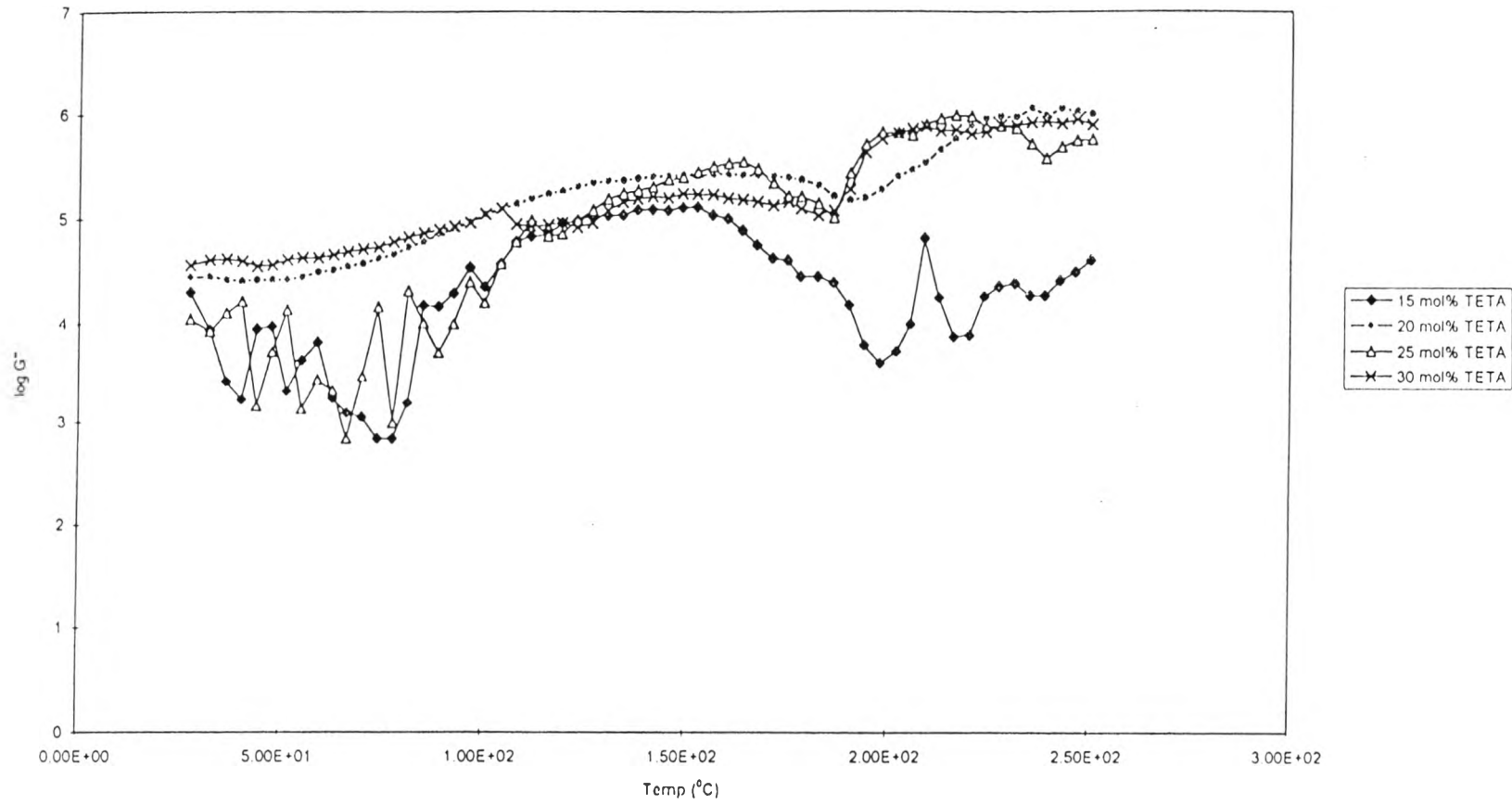


Figure 4 : Loss modulus ( $G''$ ) vs temperature of crosslinked glycolato siloxane polymer at 15 h. of crosslinking time.



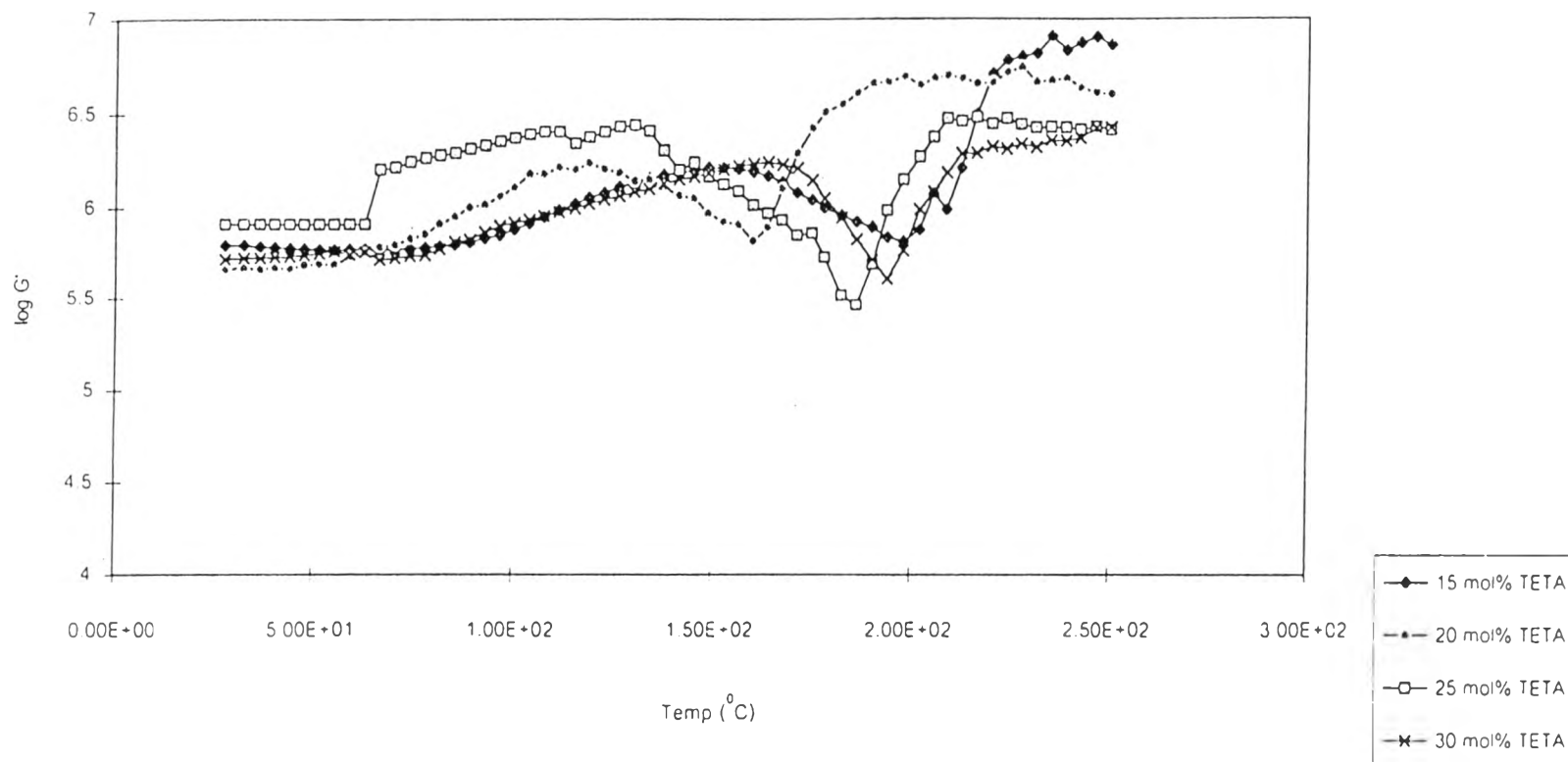


Figure 5 : Storage modulus ( $G'$ ) vs temperature of crosslinked glycolato siloxane polymer at 20 h. of crosslinking time.

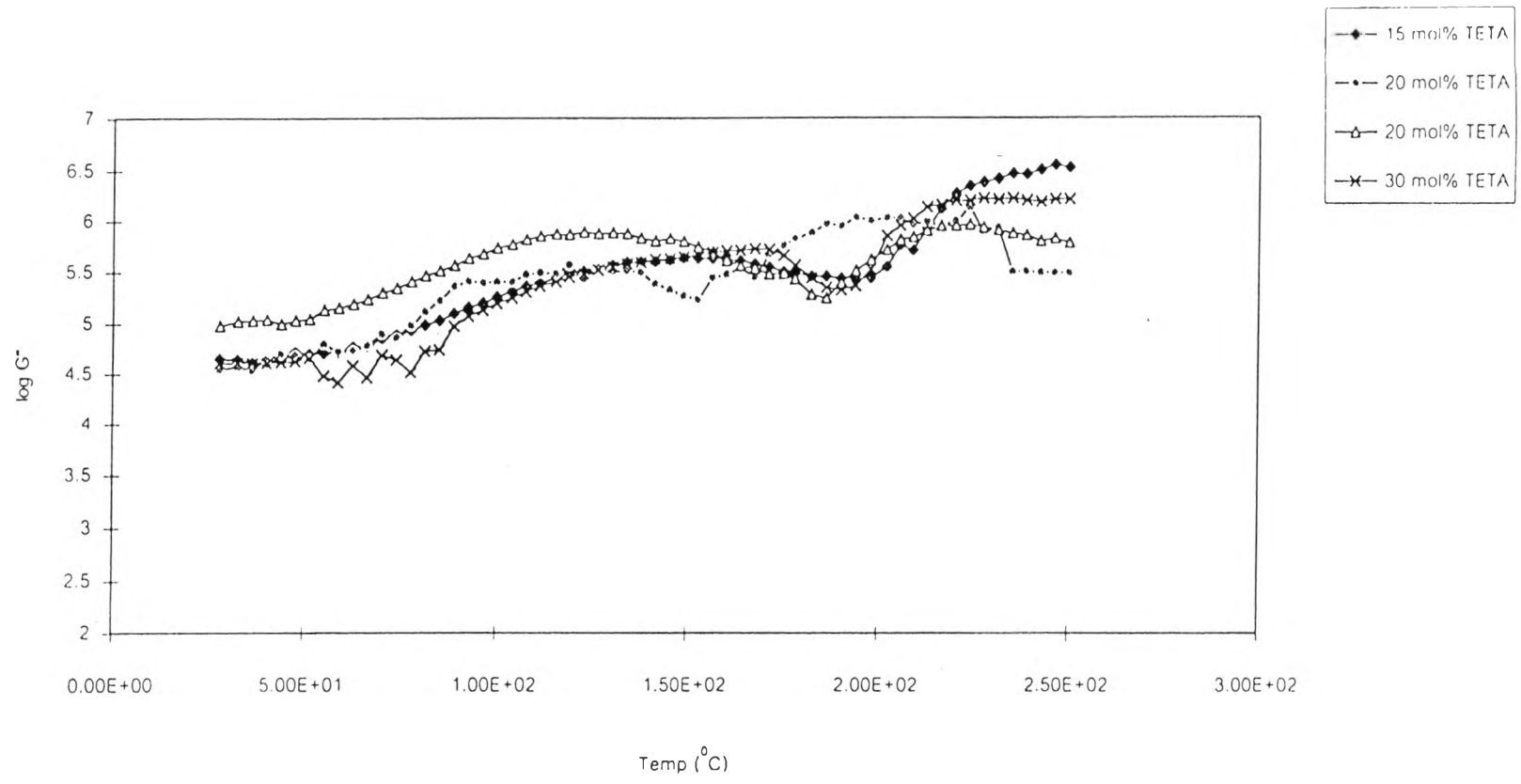


Figure 6 : Loss modulus ( $G''$ ) vs temperature of crosslinked glycolato siloxane polymer at 20 h. of crosslinking time.

## 3.2 Characterization

### 3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR is a useful technique to characterize the structure formula of the products.  $^1\text{H}$ -NMR of ethylene glycol, glycerol and crosslinked product are shown in Figures 7, 8 and 9, respectively.

$^1\text{H}$ -NMR spectrum of crosslinked product shows peaks at 3.25-3.44 ppm that splitted into multiplet due to the coupling of protons from methylene and methine groups in the product. In the product spectrum, the multiplet peaks at 3.25-3.29 ppm represent  $-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{O}-\text{Si}$  of glycolato siloxane polymer. The multiplet peaks at 3.33-3.38 ppm come from  $-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{O}-\text{Si}$  and at 3.39-3.44 ppm come from  $-\text{CH}_2-\underline{\text{C}}\text{H}-\text{O}-\text{Si}$  of glycerol in the crosslinked product. Comparing with  $^1\text{H}$ -NMR spectrum of ethylene glycol and glycerol,  $^1\text{H}$ -NMR spectrum of crosslinked product shows peaks at  $-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{O}-\text{Si}$  and  $-\text{CH}_2-\underline{\text{C}}\text{H}-\text{O}-\text{Si}$  regions at lower chemical shift. The reason for the appearing at lower chemical shift of these peaks maybe from the effect of Si in the product. Since Si atom has *d*-orbital offering free space which can let the unbonded electrons of oxygen to reside, then the amount of electrons around oxygen nuclei decreases causing the shielding effect. More applied magnetic field has to be used. As a consequence, the resonance took place at lower chemical shift. The multiplet peaks at 2.22-2.39 and 2.62-2.68 ppm display protons of TETA left in the product. A peak at 2.5 ppm is from the proton in the solvent, DMSO- $d_6$ , and the broad singlet peak at 3.8 ppm corresponds to the water absorbed in the solvent.

Figures 10, 11 and 12 demonstrate  $^{13}\text{C}$ -NMR spectra of ethylene glycol, glycerol and crosslinked product, respectively. The resulted spectrum of crosslinked polymer show peaks at 62.67 and 62.95 ppm which come from methylene group of ethylene glycol ligand. The peaks at 72.33 and 79.09 ppm

represent methylene and methine groups of glycerol ligand, respectively. Comparing the  $^{13}\text{C}$ -NMR of free EG and free glycerol, the crosslinked products show a combination of these two set of peaks. The multiplet peaks at 39 ppm is from the solvent, DMSO- $d_6$ .

Both  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR results indicate that crosslinked product in fact contains some part of glycolato siloxane group.

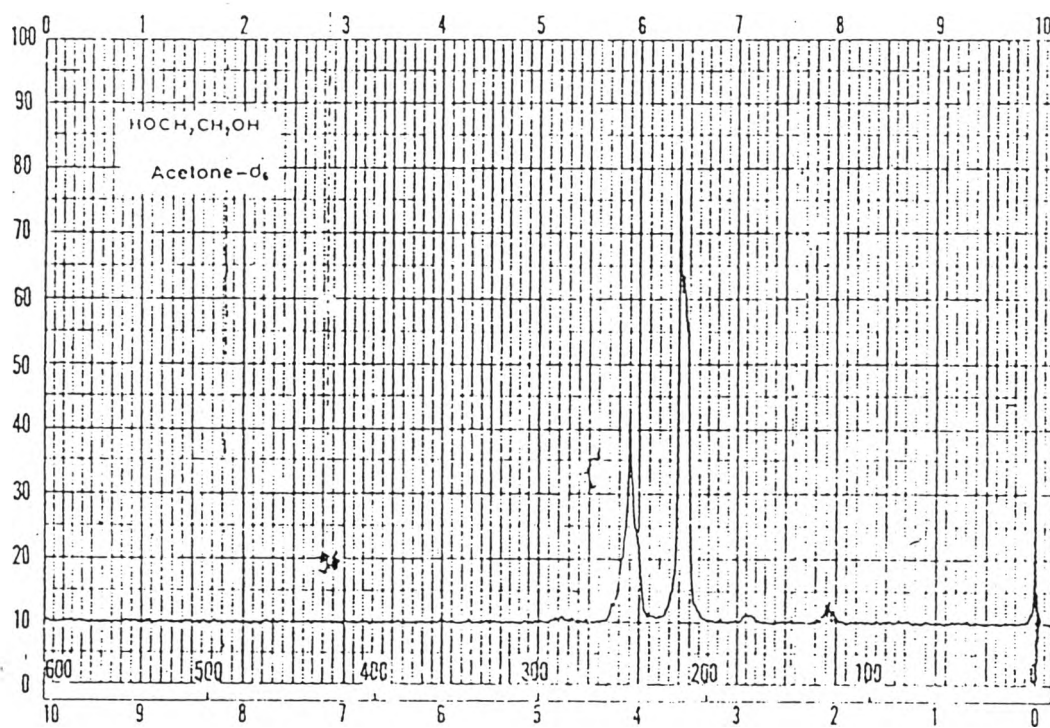


Figure 7 :  $^1\text{H-NMR}$  spectrum of ethylene glycol.

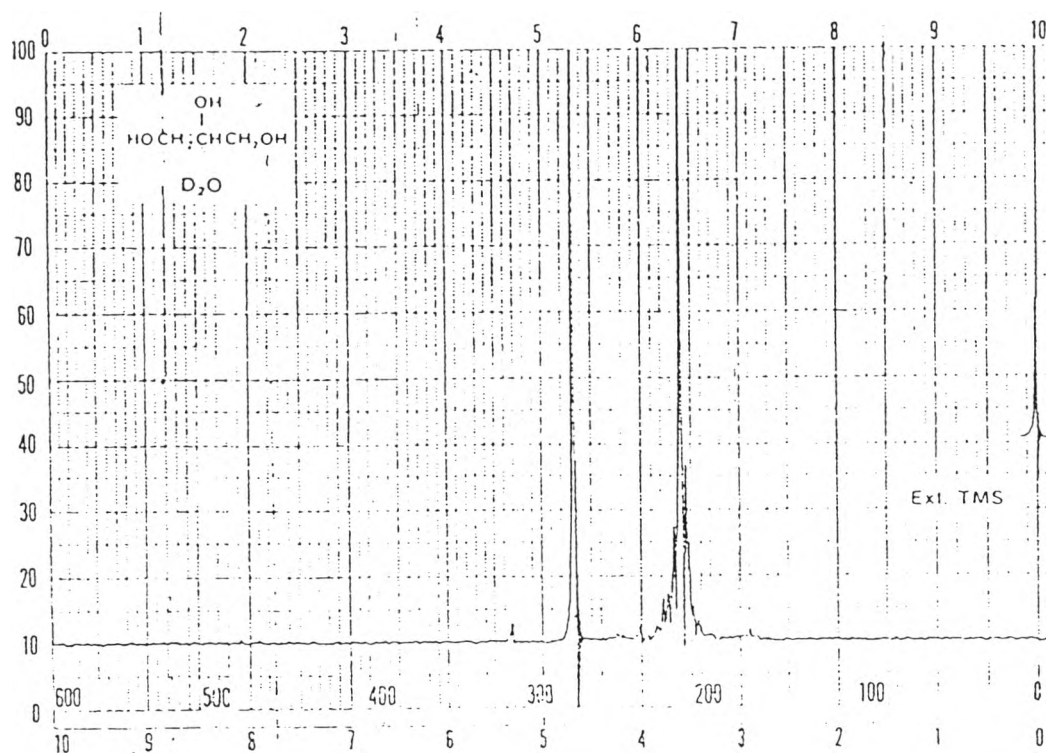


Figure 8 :  $^1\text{H-NMR}$  spectrum of glycerol.

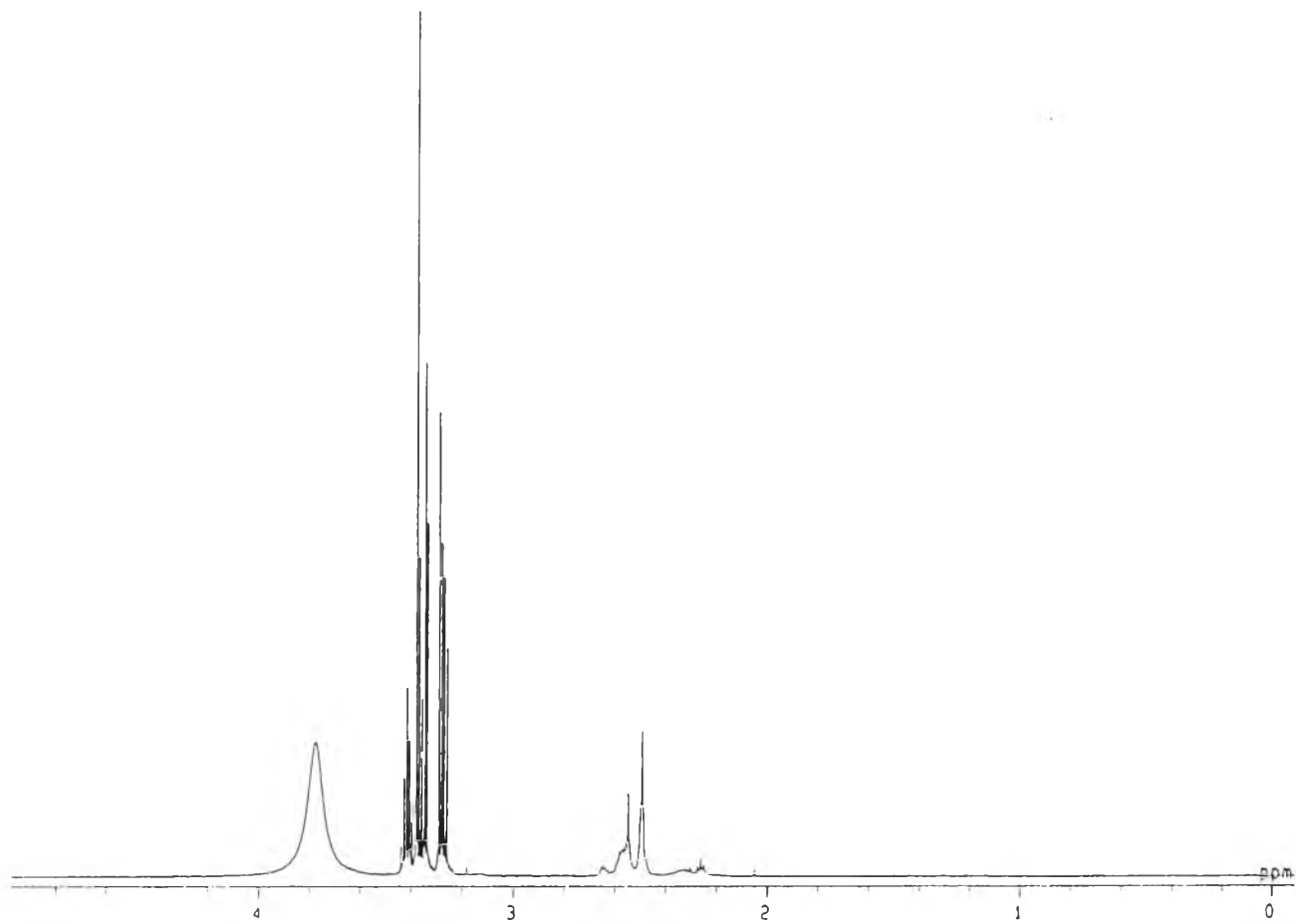


Figure 9 :  $^1\text{H-NMR}$  spectrum of crosslinked product.

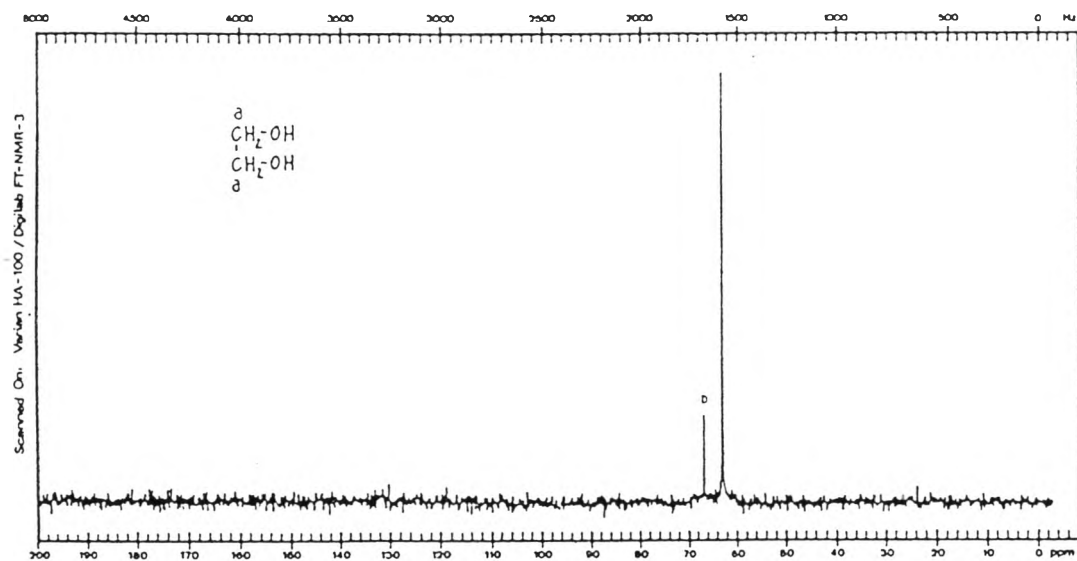


Figure 10 :  $^{13}\text{C}$ -NMR spectrum of ethylene glycol.

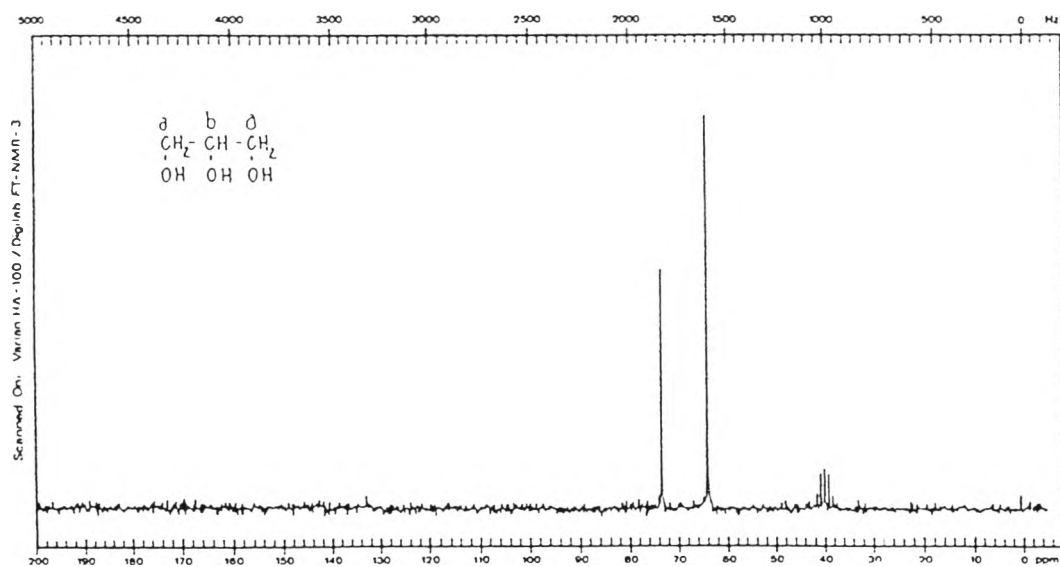


Figure 11 :  $^{13}\text{C}$ -NMR spectrum of glycerol.

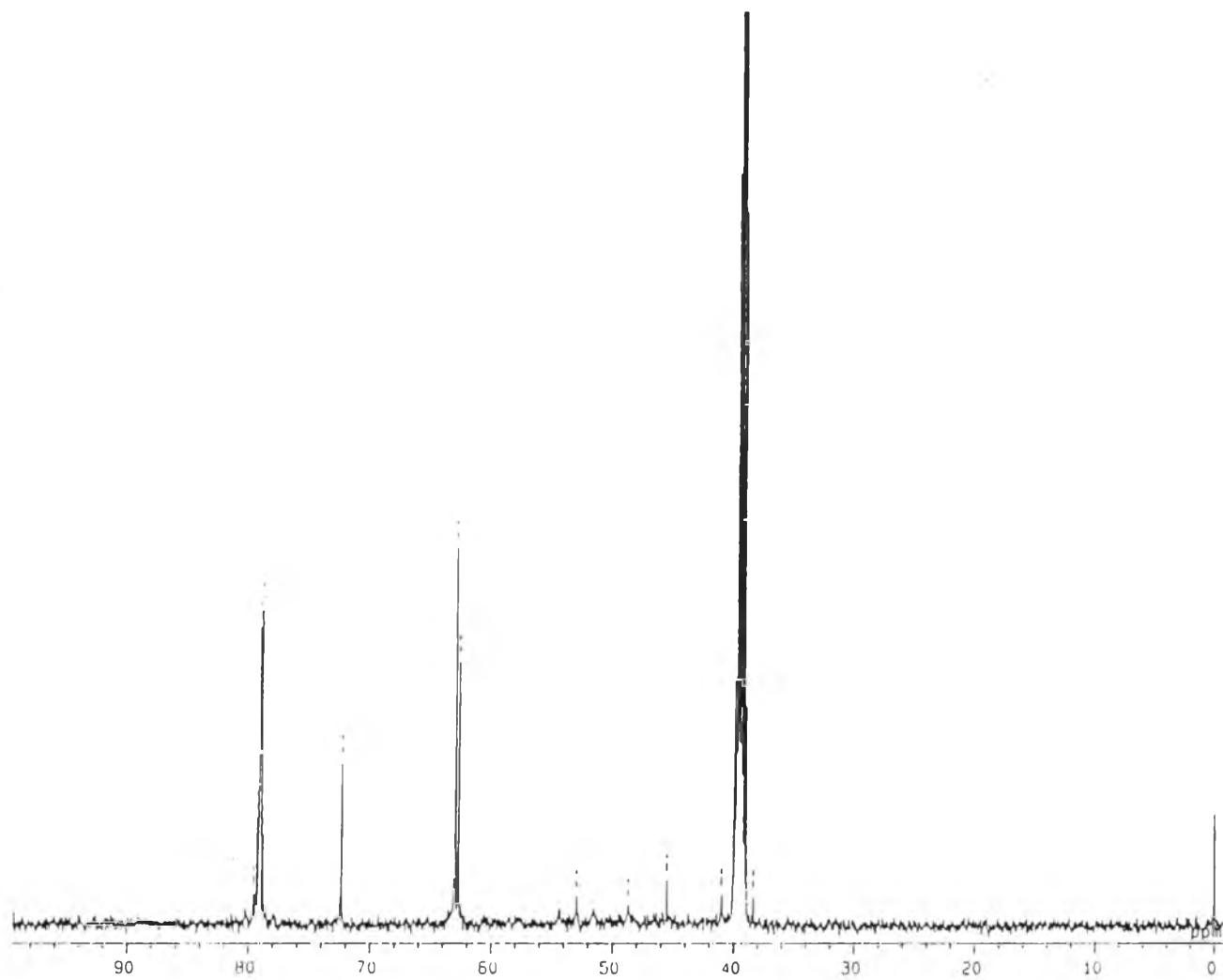


Figure 12 :  $^{13}\text{C}$ -NMR spectrum of crosslinked product.



### 3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Synthesis of glycolato siloxane polymer and crosslinked polymer give similar spectra. The spectra and the assignments glycolato siloxane polymer, crosslinked polymer (TETA concentration of 15 mol%), and all starting materials, namely, SiO<sub>2</sub>, EG and TETA, are shown in Figure 13 and Table 3.2, respectively.

From Figure 13, there are some evidence that glycolato siloxane polymer and crosslinked product are presented, since the resulting spectra show the peaks at 2845-2870 cm<sup>-1</sup> corresponding to C-H stretching of Si-EG, at 2915-2940 cm<sup>-1</sup>, corresponding to C-H stretching of Si-Glycerol, at 1084 and 879 cm<sup>-1</sup>, corresponding to Si-O-Si and Si-O-C of the product. The peak at 1084 cm<sup>-1</sup> which comes from Si-O-Si bond, indicates that the hydrolysis occurs while glycerol is exchanging with EG.

From Figures 14, 15, and 16, the FTIR spectra of crosslinked product do not show significant variations with different crosslinking reaction times, or TETA concentrations. This suggests that the functional groups contained in the crosslinked products cannot be quantitative analysed by FTIR technique.

The FTIR spectra of crosslinked products (see Figures 14-16) show strong intensity absorption peak of Si-O-Si and Si-O-C stretching at 1100 cm<sup>-1</sup> and a low intensity peak at 806 cm<sup>-1</sup>. The peak at 490 cm<sup>-1</sup> also corresponds to Si-O-Si stretching. As compared to the spectra of EG and glycerol, the crosslinked products also demonstrate the peaks at 1650 cm<sup>-1</sup>, corresponding to O-H bending of Si-EG, at 1250-1350 cm<sup>-1</sup>, corresponding to O-H bending of Si-Glycerol, at 800-1200 cm<sup>-1</sup> and 1440-1480 cm<sup>-1</sup>, corresponding to C-C and C-H bendings of Si-EG and Si-Glycerol, respectively. The peak at 2845-2870 cm<sup>-1</sup> is from C-H stretching of Si-EG and at 2915-2940 cm<sup>-1</sup> is from C-H stretching of Si-Glycerol. The broad peak at

3300-3640  $\text{cm}^{-1}$  represents the bonded -OH stretching of Si-EG and Si-Glycerol.

Table 3.2 : Assignment of infrared spectra of reactants and product

Characterization	SiO <sub>2</sub>	EG	TETA	Si-EG	Si-Glycerol
Bonded -OH stretching	-	3700-3100 $\text{cm}^{-1}$ (strong, broad)	-	3600-3300 $\text{cm}^{-1}$ (strong, broad)	3640-3630 $\text{cm}^{-1}$ (strong, broad)
NH <sub>2</sub> stretching	-	-	3600-3300 $\text{cm}^{-1}$ (strong, broad)	-	-
>NH stretching	-	-	3450-3300 $\text{cm}^{-1}$ (1 band)	-	-
C-H stretching	-	2960-2890 $\text{cm}^{-1}$ (medium, doublet)	2843-2845 $\text{cm}^{-1}$ (medium, doublet)	2870-2845 $\text{cm}^{-1}$ (weak, doublet)	2940-2915 $\text{cm}^{-1}$ (weak, doublet)
C-H bending	-	1450 $\text{cm}^{-1}$ (weak, sharp)	1469 $\text{cm}^{-1}$ (medium, sharp)	1480-1440 $\text{cm}^{-1}$ (weak, sharp)	1480-1440 $\text{cm}^{-1}$
N-H bending	-	-	1650-1550 $\text{cm}^{-1}$ (medium, sharp)	-	-
O-H bending	-	1650 $\text{cm}^{-1}$ (medium, sharp)	-	1650 $\text{cm}^{-1}$ (medium, sharp)	1350-1250 $\text{cm}^{-1}$ (medium, sharp)
C-C stretching	-	1200-800 $\text{cm}^{-1}$ (weak, broad)	-	1200-800 $\text{cm}^{-1}$ (weak, broad)	1200-800 $\text{cm}^{-1}$ (weak, broad)
C-O stretching	-	1030-1070 $\text{cm}^{-1}$ (strong)	-	1030-1070 $\text{cm}^{-1}$ (strong)	1120-1080 $\text{cm}^{-1}$
Si-O-Si <sup>+</sup> Si-O-C stretching	1100 (broad) 806 (weak) 490 (weak)	-	-	1084 (broad) 879 (weak)	1084 (broad) 879 (weak)
N-H out of plane bending	-	-	815-720 $\text{cm}^{-1}$ (weak, broad)	-	-

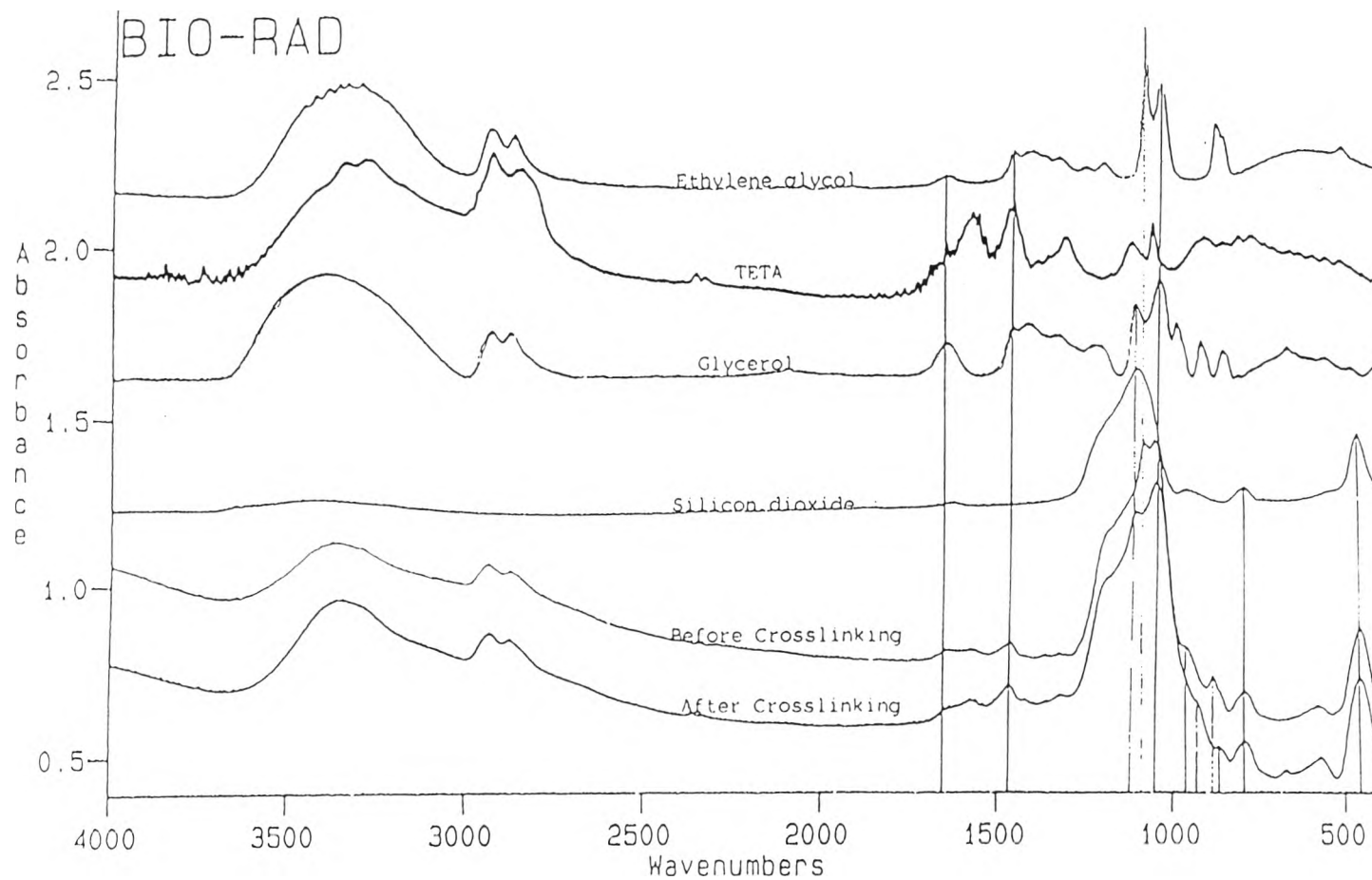


Figure 13 : The FTIR spectra of glycolato siloxane polymer, their crosslinked polymer and all starting materials.

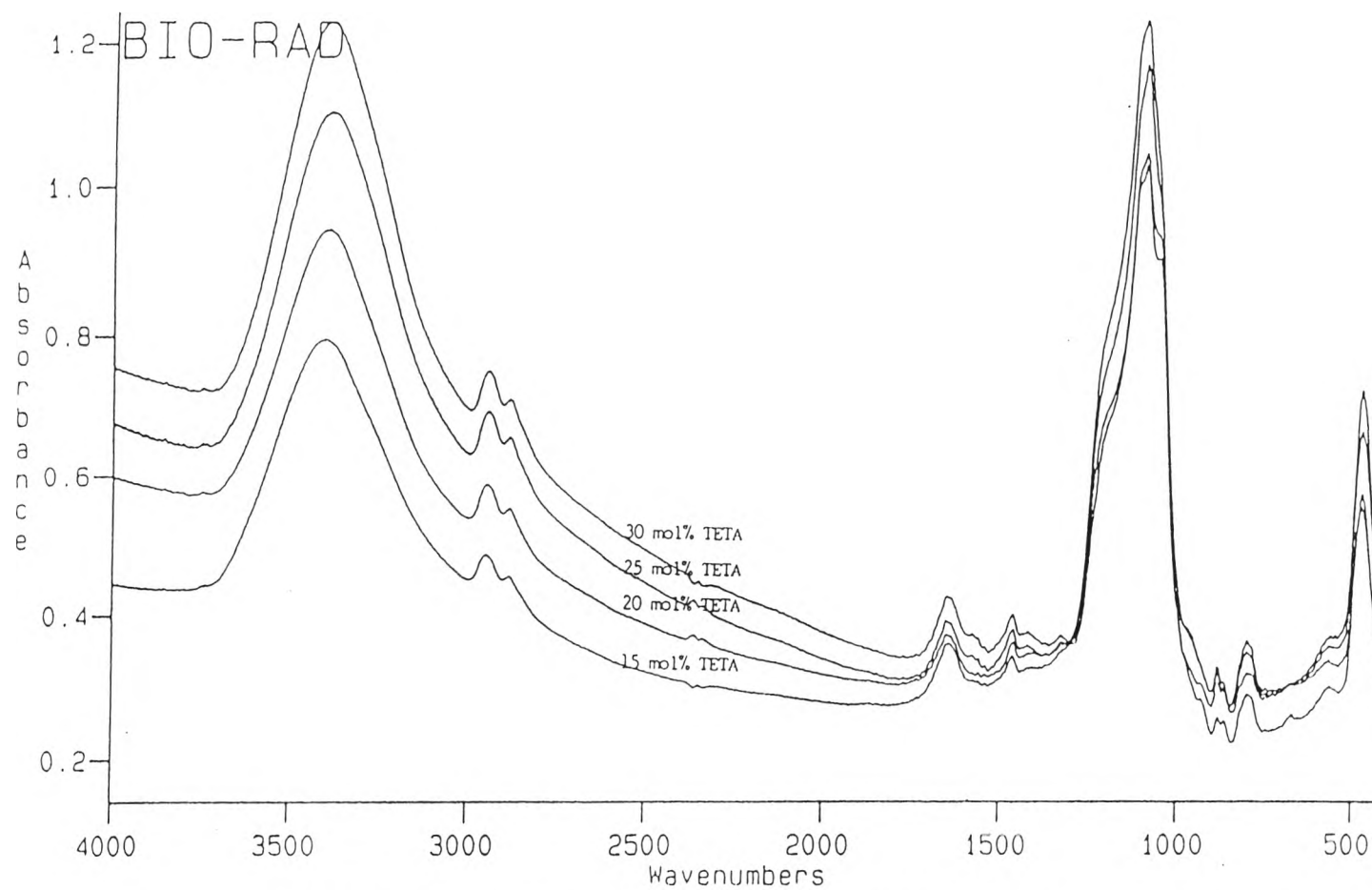


Figure 14 : The FTIR spectra of crosslinked glycolato siloxane polymer at at 10 h. of crosslinking reaction time.

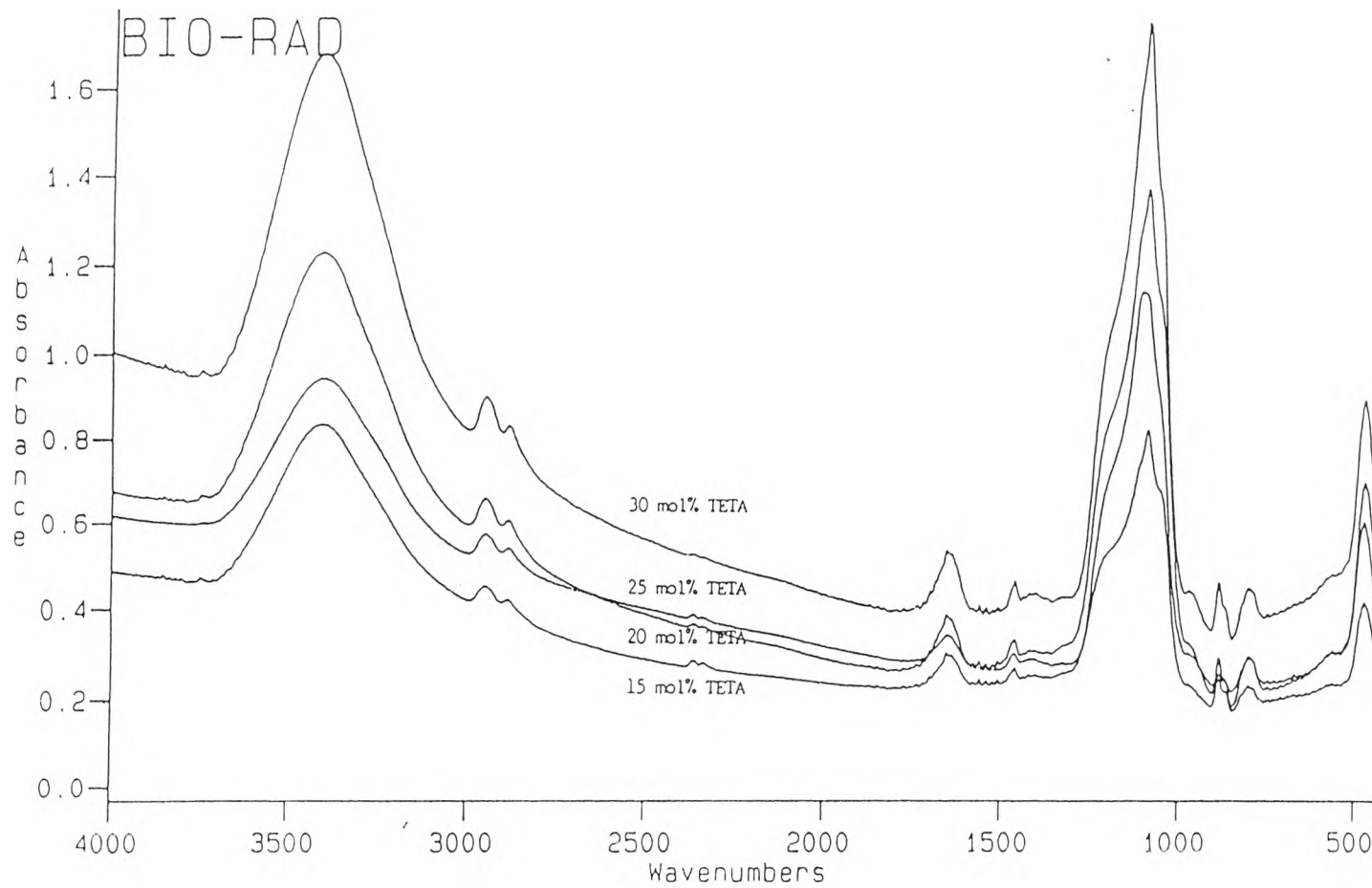


Figure 15 : The FTIR spectra of crosslinked glycolato siloxane polymer at 15 h. of crosslinking reaction time.



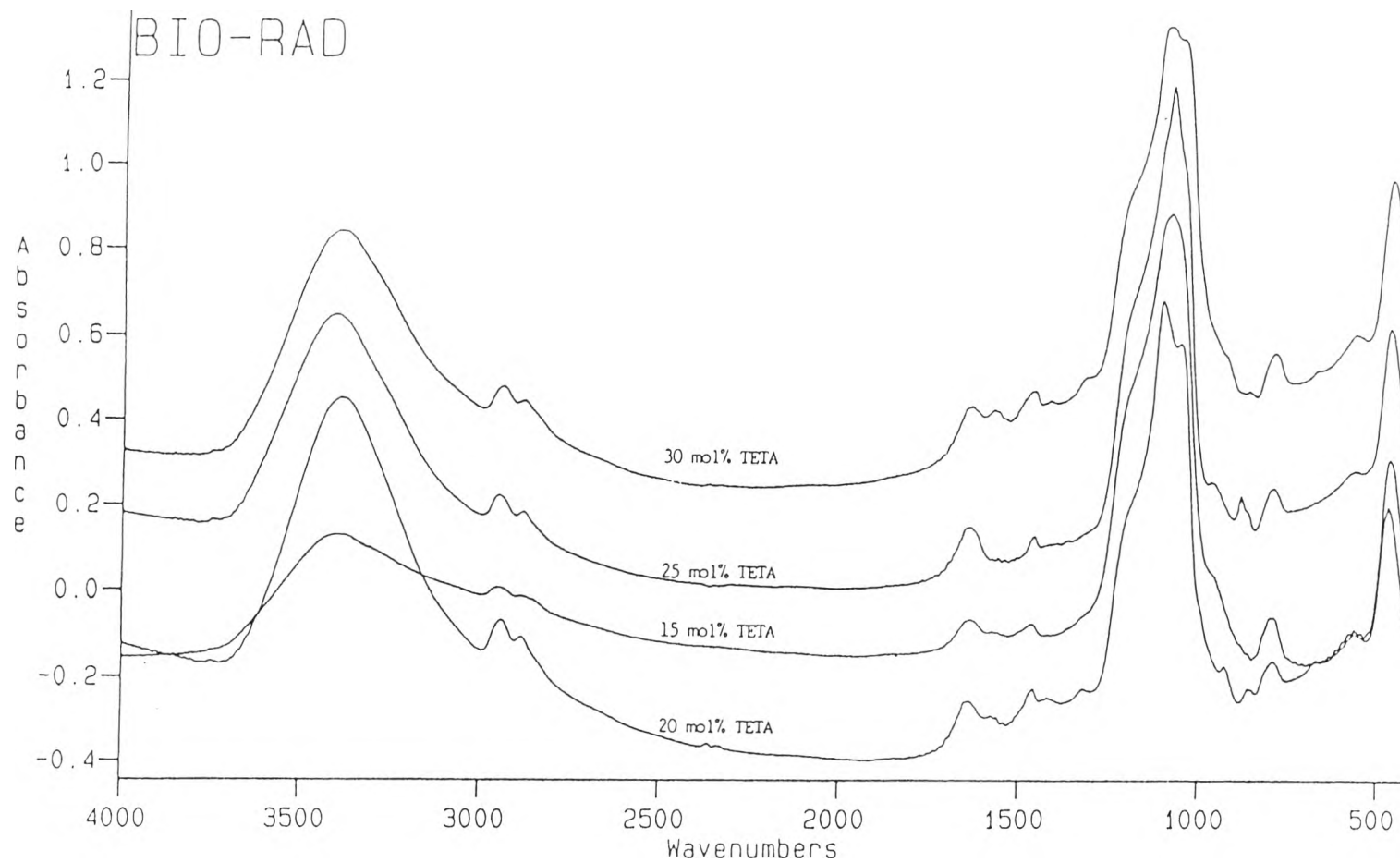


Figure 16 : The FTIR spectra of crosslinked glycolato siloxane polymer at  
at 20 h. of crosslinking reaction time.

### 3.2.3 Thermogravimetric Analysis (TGA)

As discussed previously, all TGA studies were run in  $N_2$  and  $O_2$  at the ramp rate of  $10^\circ C/min$ . TETA concentration of 15, 20, 25 and 30 mol% crosslinked polymers at each crosslinking reaction time gave TGA profiles with the relatively high ceramic yields. This could be interpreted as networks of polymers since the system had excess glycerol and was run in the presence of TETA.

The variation of TETA concentration and crosslinking reaction time had effect on ceramic yields (Figures 17-19). Before the crosslinking step, EG reacted with  $SiO_2$  in the presence of TETA, as a base, to form  $Si(eg)_2$ . If there were some water left in the product, water could hydrolyze some EG and glycerol ligands in the polymer molecules to form Si-O-Si bonds which caused the obtained ceramic yields to be higher than the theoretical ones. After glycerol was added, it exchanged with some EG ligands in  $Si(eg)_2$  groups to give  $Si(gly)_2$  molecules which then crosslinked to form a network polymer. Then the ceramic yield dropped because the amount of organic ligands in crosslinked polymers was higher than before crosslinking step. After the reaction was continued, the ceramic yield increased again since some glycerol linkages broke from the network and form acrolein molecules which have low boiling point and evaporated away.

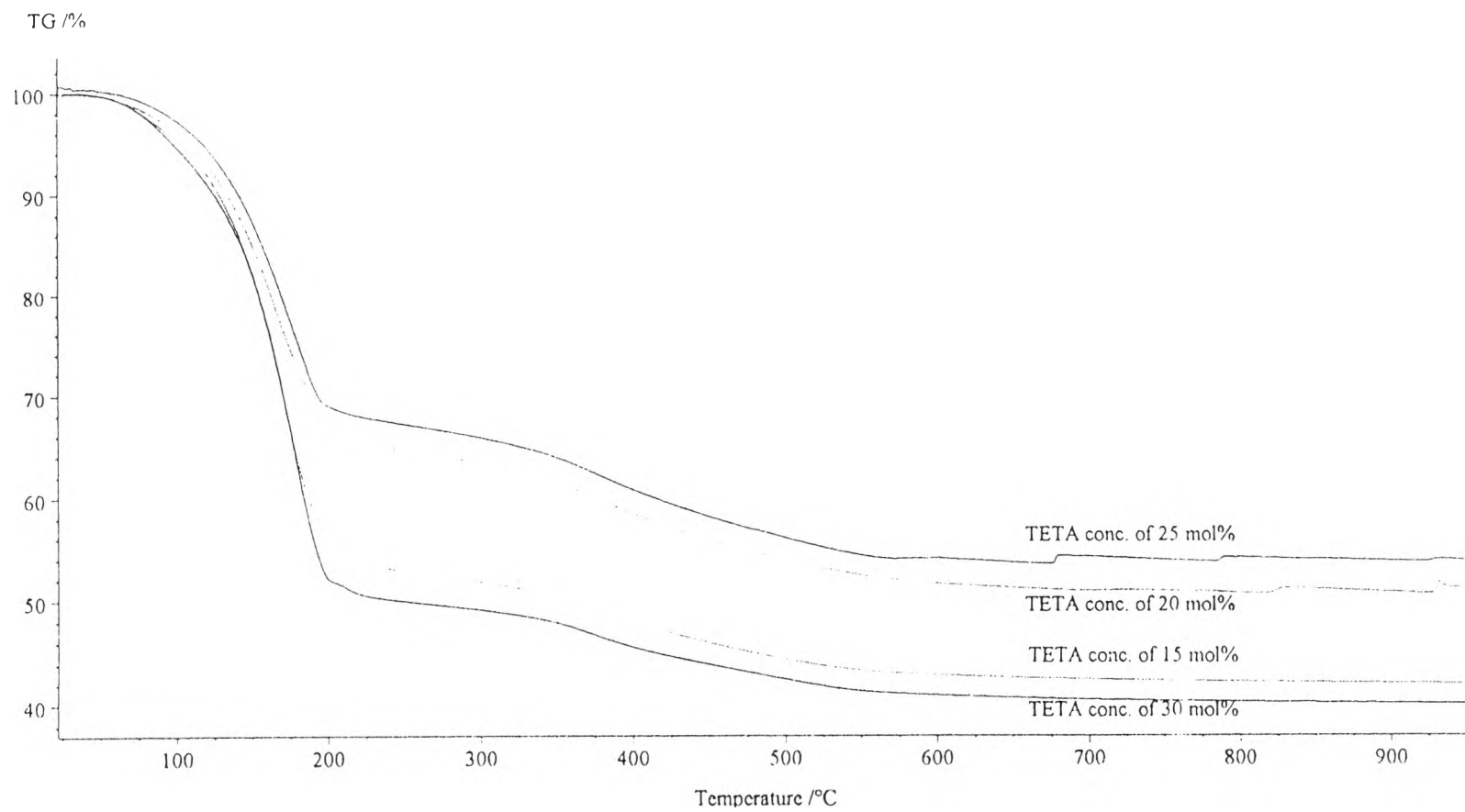


Figure 17 : The TGA profiles of crosslinked polymer at different TETA concentration under at 10 hr. of crosslinking Time.



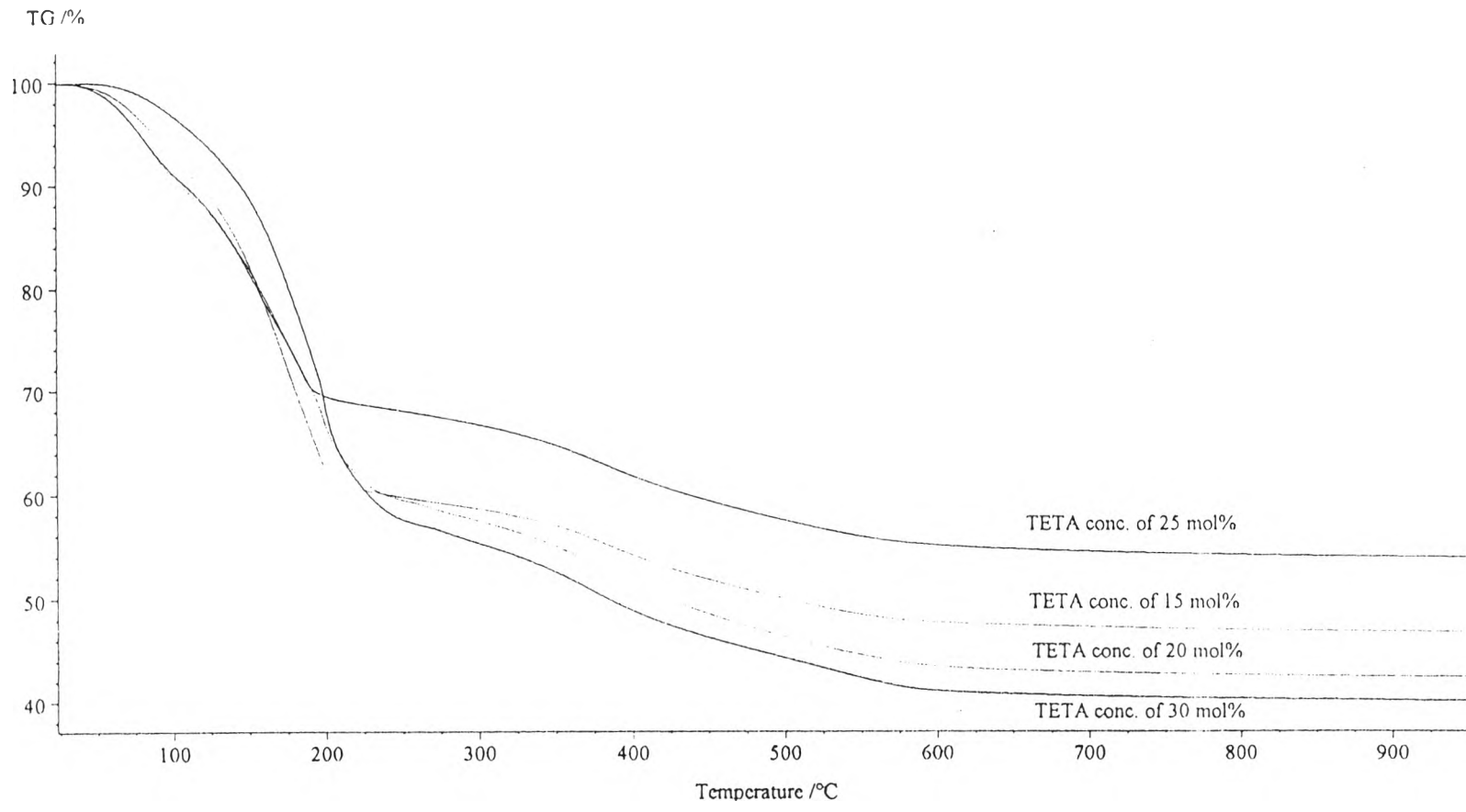


Figure 18 : The TGA profiles of crosslinked polymer at different TETA concentration under at 15 hr. of crosslinking Time.

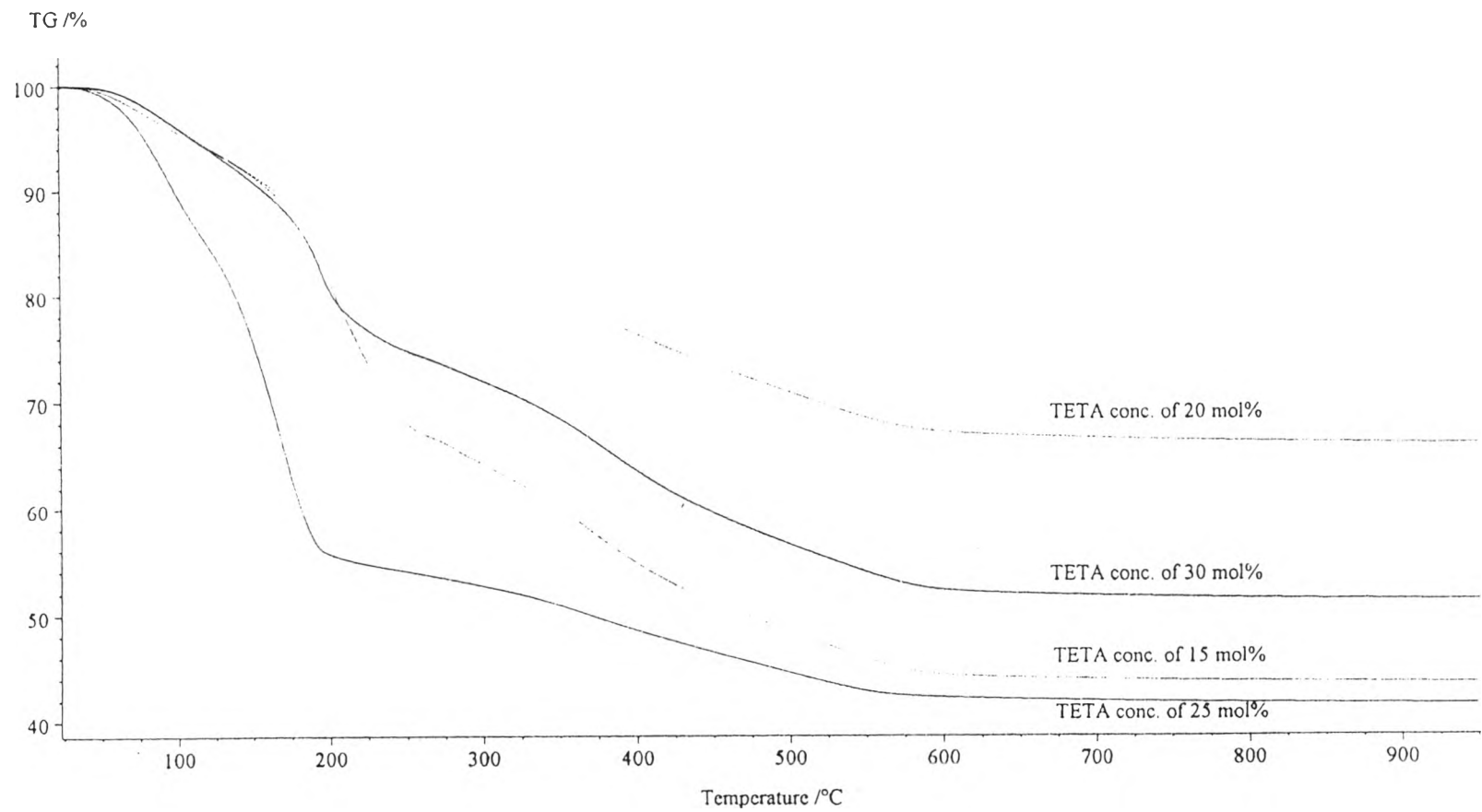


Figure 19 : The TGA profiles of crosslinked polymer at different TETA concentration under at 20 hr. of crosslinking Time.