

CHAPTER IV

RESULTS AND DISCUSSUIN

The modification of natural rubber via graft copolymerization is to prepare a product that possesses, at least, some better properties than those of the unmodified natural rubber. In addition, it is conceivable that the graft copolymer might show novel properties due to the highly ambivalent nature of the rubber backbone and grafted side chain. The graft copolymerization of methyl methacrylate onto natural rubber was prepared by emulsion polymerization in which reaction parameters of initiator concentration, reaction temperature, monomer concentration and reaction time were taken into account. Various blends of grafted natural rubber and poly (methyl methacrylate) were prepared by a two roll-mill and the mechanical properties of the blends were investigated.

4.1 Properties of Natural Rubber Latex

The natural rubber latex was obtained from Revertex (Thailand) Ltd. has the properties as shown in Table 4.1.

Table 4.1 The properties of natural rubber latex (High Ammonia).

Properties	Test Results
Total Solid Content, %	62.65
Dry Rubber Content, %	61.20
Non Rubber Solids, %	1.45
Ammonia Content (on Total Weight), %	0.67
Ammonia Content (on Water Phase), %	1.79
pH value	10.60
KOH Number	0.48
Volatile Fatty Acid Number (V.F.A.)	0.0155
Mechanical Stability Time @ 55% TS., Sec	60
Specific Gravity at 25°C	0.95
Magnesium (ppm)	25

Remark : Free from pentachlorophenol.

4.2 Preparation of Grafted Natural Rubber

The work described here consists of a study of the graft copolymerization of methyl methacrylate in natural rubber latex by emulsion polymerization technique and using potassium persulfate as initiator. This study examines the dependence of percentage conversion, percentage grafted natural rubber and percentage grafting efficiency on initiator concentration, reaction temperature, monomer concentration, and reaction time.

The appropriate conditions which yielded high percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency were investigated.

4.2.1 Effect of Initiator Concentration

The graft copolymerization of methyl methacrylate onto natural rubber was carried varying the concentration of initiator and reaction temperature over a wide range. The effects of initiator concentration at various temperatures on the percentage conversion, percentage grafted natural rubber and percentage grafting efficiency are shown in Tables 4.2 - 4.3 and Figures 4.1 - 4.7. The details of all data and calculations are shown in Appendix A. The parameters of graft copolymerization were obtained as follows:

- Rubber content : 100 phr
- Monomer concentration : 100 phr
- Initiator concentration : 0.50-2.00 phr
- Reaction temperature : 50-70°C
- Reaction time : 8 hr.

Figures 4.1b - 4.4b show the effect of initiator concentration on the percentage conversion at different temperatures. In Figure 4.5, the percentage conversion increases as the initiator concentration increases at every temperature investigated. Initially, the increase in the initiator concentration produces more free radicals, therefore, the percentage conversion increase. At the higher initiator concentrations, an abundance of initiator radical is produced and radical recombination can occur to some extent slightly increase the percentage conversion. The effect of initiator concentration on the percentage grafted natural rubber, percentage free NR, and percentage free PMMA at different temperatures are shown in Figures 4.1a – 4.4a. In Figure 4.1a, increasing initiator concentration up to 0.75 phr is accompanied by a significant increase in percentage grafted natural rubber while further increase causes a marked fall in the percentage grafted natural rubber. It can be seen that as the percent grafted natural rubber increases, percentage free NR and percentage free PMMA decrease at every temperature investigated. When more concentration of the initiator is used excessive radicals react with each other leading

to a faster rate of termination. Beyond the limit of the initiator concentration, percentage grafted natural rubber does not increase but rather slightly decrease. The highest percentage grafted natural rubber and percentage grafting efficiency were observed at the reaction temperatures of 55°C and the initiator concentration of 0.75 phr as shown in Figures 4.6 and 4.7.

4.2.2 Effect of Reaction Temperature

The effects of reaction temperature on the percentage conversion, percentage grafted natural rubber and percentage grafting efficiency are shown in Table 4.4 and Figures 4.8 - 4.10. The details of all data and calculations are shown in Appendix A. The parameters of graft copolymerization were obtained as follows:

- Rubber content : 100 phr
- Monomer concentration : 100 phr
- Initiator concentration : 0.75, 1.00 phr
- Reaction temperature : 50-70°C
- Reaction time : 8 hr.

In Figure 4.8, the higher temperature results in higher percentage conversion, because increasing temperature, decomposition of initiator increases, it result an increased number of free radicals and the rate of polymerization. The effect of temperature on percentage grafted natural rubber and percentage grafting efficiency are shown in Figures 4.8 - 4.12, both results are decreased when the polymerizing temperature was higher than 55°C. The initiator decomposition increased with the increasing temperature to give instantaneously abundance of free radicals. The radicals underwent either recombination, or other side reaction, the initiator efficiency is thus reduced.

Table 4.2 Effect of the initiator concentration on the percentage conversion, percentage grafting efficiency, and percentage grafted natural rubber at 50-55°C; MMA 100 phr, and time 8 hr.

	50°C					55°C				
	Initiator concentration, phr									
	0.50	0.75	1.00	1.50	2.00	0.50	0.75	1.00	1.50	2.00
Conversion (%)	37.5	41.2	52.4	56.9	65.4	67.4	75.9	79.9	82.1	82.3
Grafting efficiency (%)	39.6	54.8	53.5	47.5	47.4	60.9	64.1	59.9	51.0	50.7
Graft properties										
Grafted natural rubber (%)	40.0	54.7	53.9	48.1	44.7	56.4	57.9	54.0	45.5	45.3
Free NR (%)	43.5	32.1	30.1	32.8	34.5	27.9	26.6	28.1	32.4	32.5
Free PMMA (%)	16.5	13.1	16.0	19.1	20.8	15.7	15.4	17.8	22.1	22.2

14580579

Table 4.3 Effect of the initiator concentration on the percentage conversion, percentage grafting efficiency, and percentage grafted natural rubber at 60-70°C; MMA 100 phr, and time 8 hr.

	60°C					70°C				
	Initiator concentration, phr									
	0.50	0.75	1.00	1.50	2.00	0.50	0.75	1.00	1.50	2.00
Conversion (%)	76.2	81.3	81.3	84.6	85.2	80.2	85.5	85.0	86.0	86.5
Grafting efficiency (%)	52.0	56.9	56.3	52.2	51.2	41.9	50.1	46.9	38.7	40.1
Graft properties										
Grafted natural rubber (%)	45.8	52.9	51.4	46.9	46.1	37.4	48.1	39.8	30.7	33.9
Free NR (%)	33.4	27.8	29.0	31.2	31.4	36.8	28.9	35.9	41.0	41.3
Free PMMA (%)	20.8	19.3	19.6	21.9	22.5	25.9	23.0	24.4	28.3	27.8

Table 4.4 Effect of the reaction temperature on the percentage conversion, percentage grafting efficiency, and percentage grafted natural rubber; MMA 100 phr, initiator concentration 0.75-1.00 phr, and time 8 hr.

	Initiator 0.75 phr				Initiator 1.00 phr			
	Reaction temperature, °C							
	50	55	60	70	50	55	60	70
Conversion (%)	41.2	75.9	81.3	85.8	52.4	79.9	81.3	85.0
Grafting efficiency (%)	54.8	64.1	56.9	50.1	53.5	59.9	56.3	46.9
Graft properties								
Grafted natural rubber (%)	54.7	57.9	52.9	48.1	53.9	54.0	51.4	39.8
Free NR (%)	32.1	26.6	27.8	28.9	30.1	28.1	29.0	35.9
Free PMMA (%)	13.1	15.4	19.3	23.0	16.0	17.8	19.6	24.4

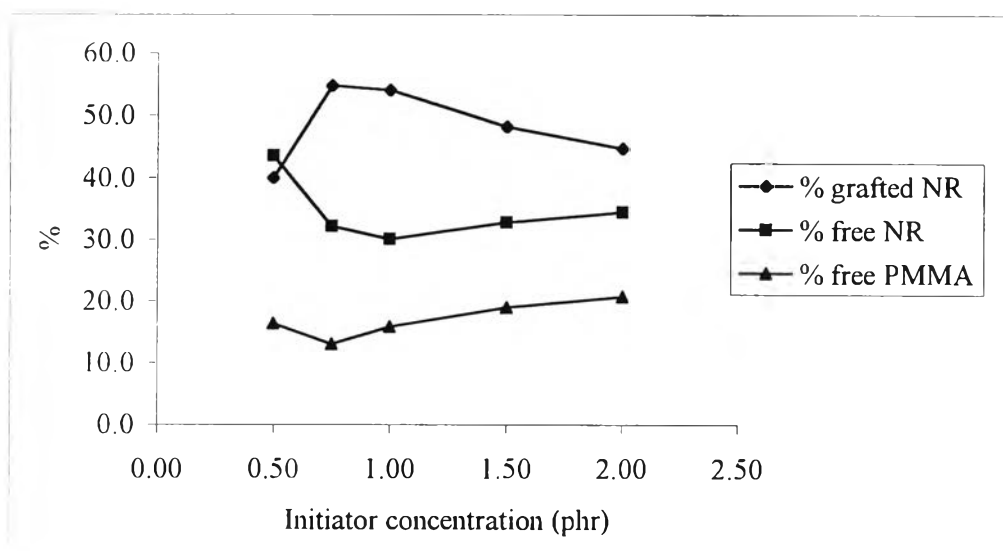


Figure 4.1a Effect of the initiator concentration on the percentage grafted natural rubber, percentage free NR, and percentage free PMMA at 50°C; MMA 100 phr and time 8 hr.

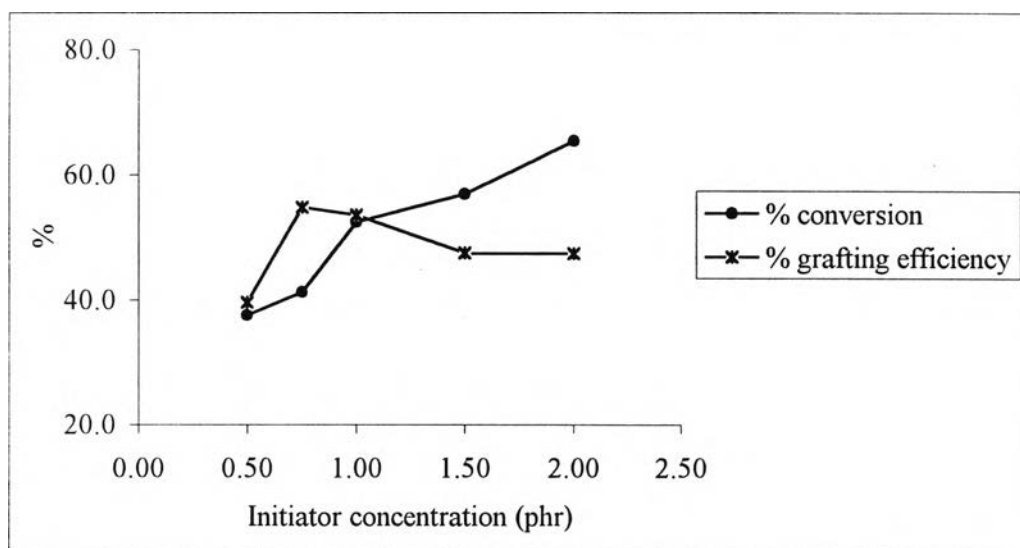


Figure 4.1b Effect of the initiator concentration on the percentage conversion and percentage grafting efficiency at 50°C; MMA 100 phr and time 8 hr.

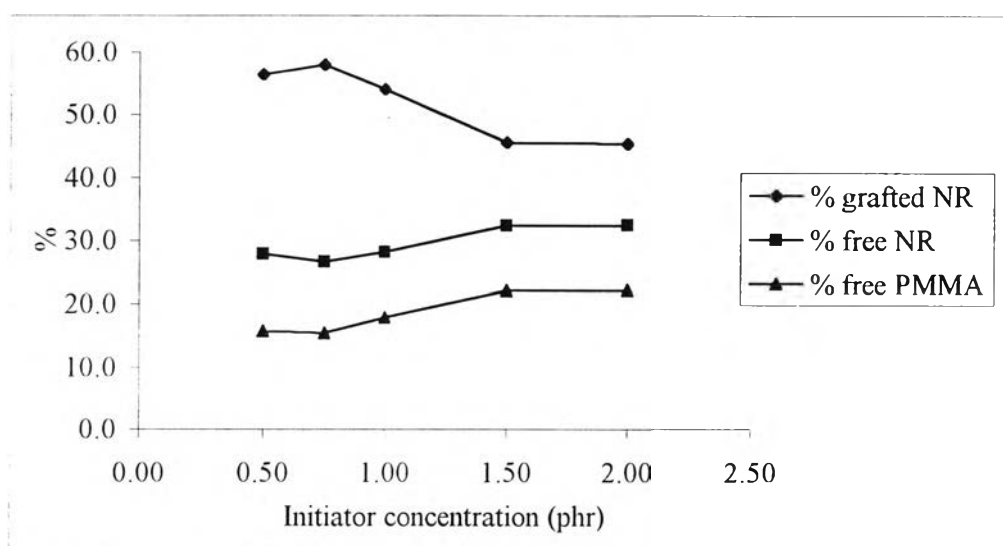


Figure 4.2a Effect of the initiator concentration on the percentage grafted natural rubber, percentage free NR, and percentage free PMMA at 55°C; MMA 100 phr and time 8 hr.

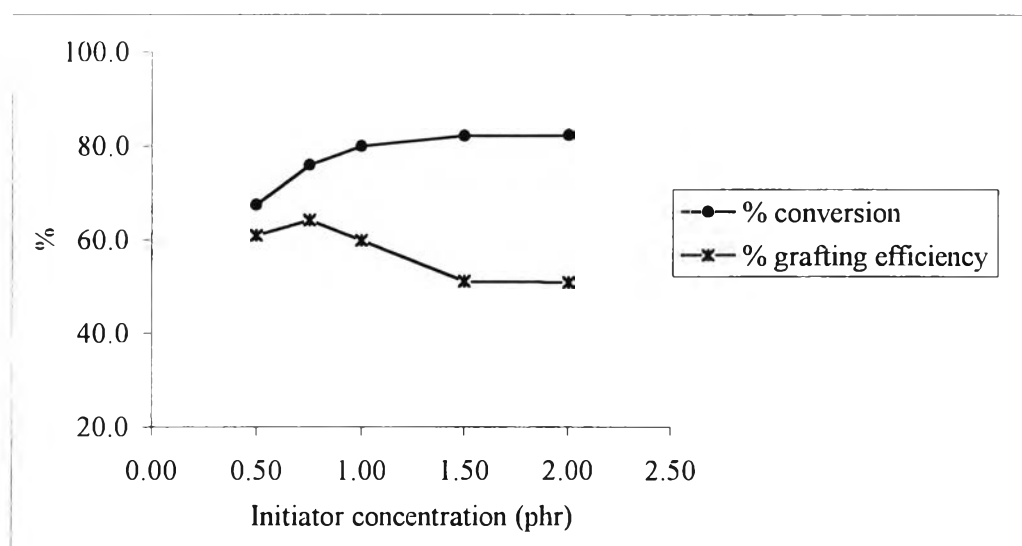


Figure 4.2b Effect of the initiator concentration on the percentage conversion and percentage grafting efficiency at 55°C; MMA 100 phr and time 8 hr.

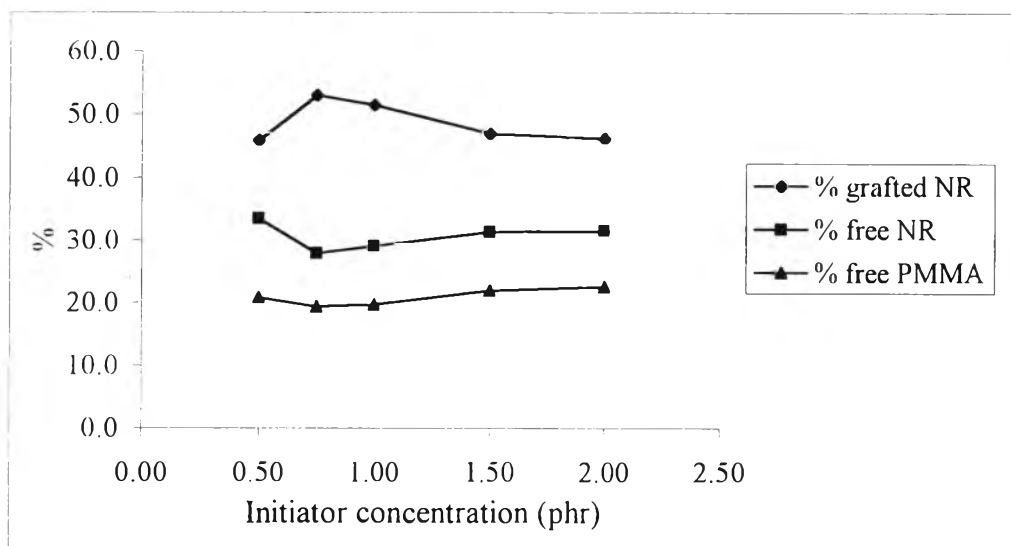


Figure 4.3a Effect of the initiator concentration on the percentage grafted natural rubber, percentage free NR, and percentage free PMMA at 60°C; MMA 100 phr and time 8 hr.

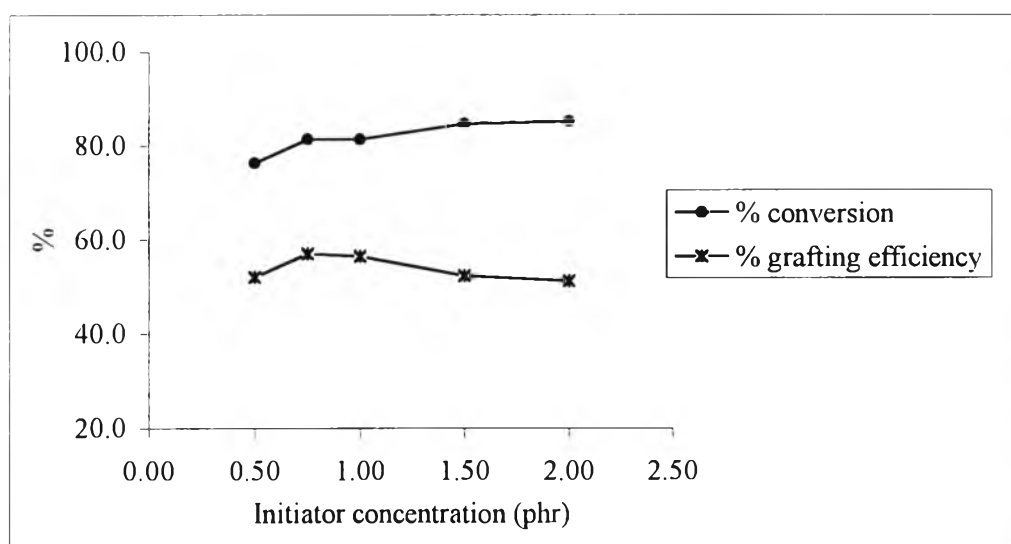


Figure 4.3b Effect of the initiator concentration on the percentage conversion and percentage grafting efficiency at 60°C; MMA 100 phr and time 8 hr.

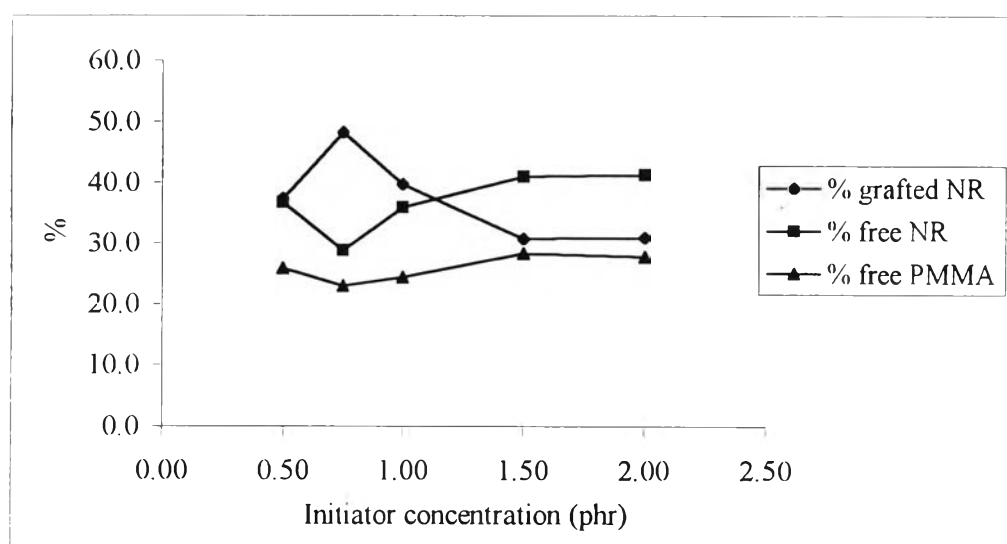


Figure 4.4a Effect of the initiator concentration on the percentage grafted natural rubber, percentage free NR, and percentage free PMMA at 70°C; MMA 100 phr and time 8 hr.

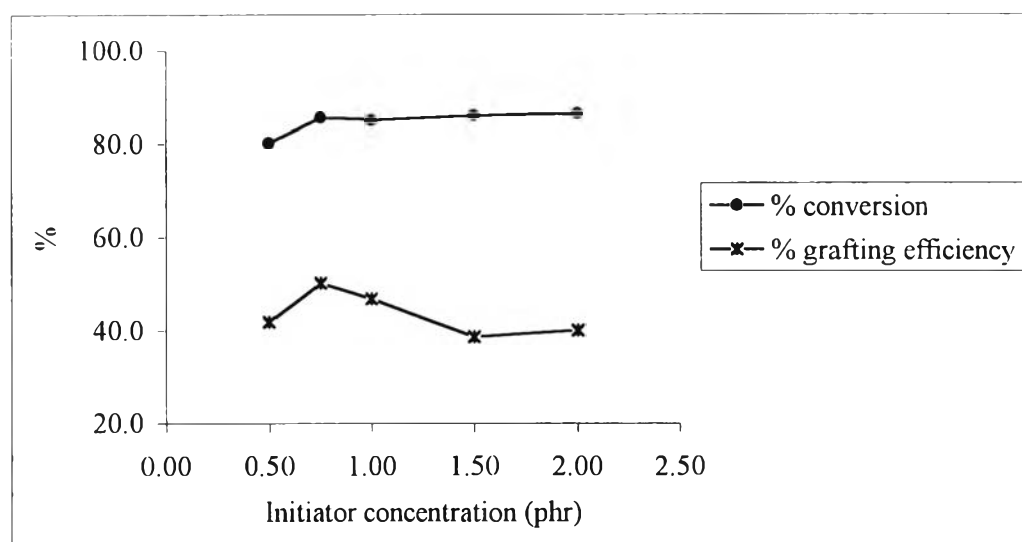


Figure 4.4b Effect of the initiator concentration on the percentage conversion and percentage grafting efficiency at 70°C; MMA 100 phr and time 8 hr.

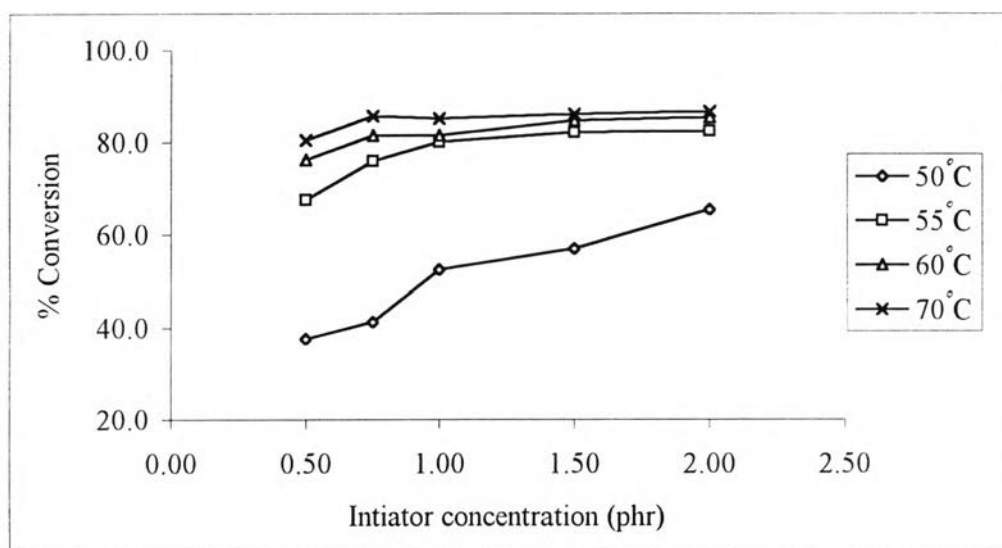


Figure 4.5 Effect of the initiator concentration on the percentage conversion at 50-70°C; MMA 100 phr and time 8 hr.

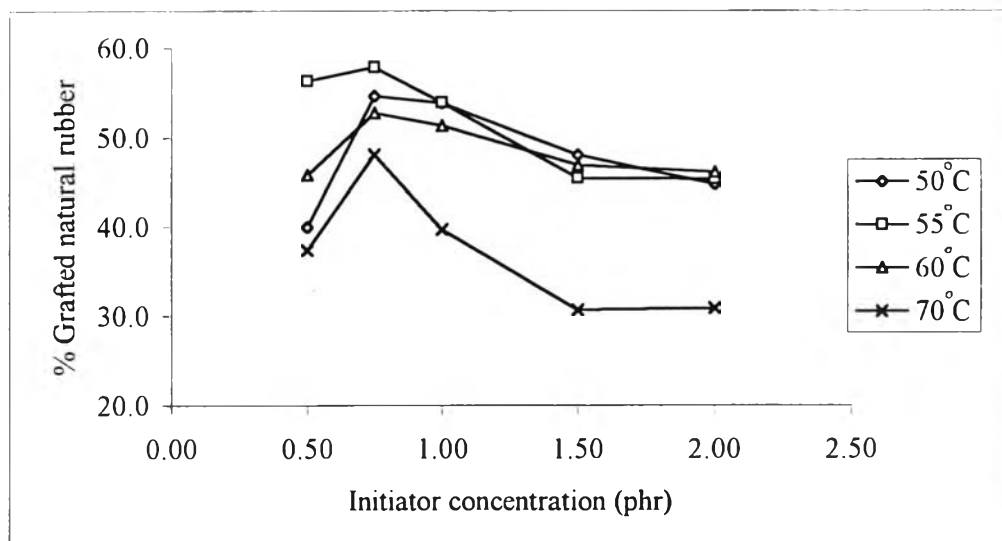


Figure 4.6 Effect of the initiator concentration on the percentage grafted natural rubber at 50-70°C; MMA 100 phr and time 8 hr.

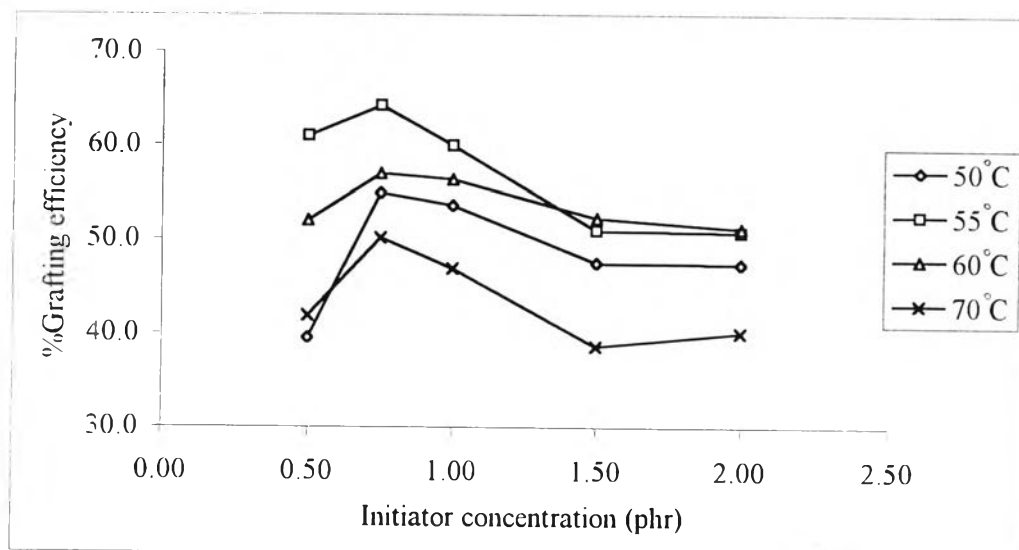


Figure 4.7 Effect of the initiator concentration on the percentage grafting efficiency at 50-70°C; MMA 100 phr and time 8 hr.

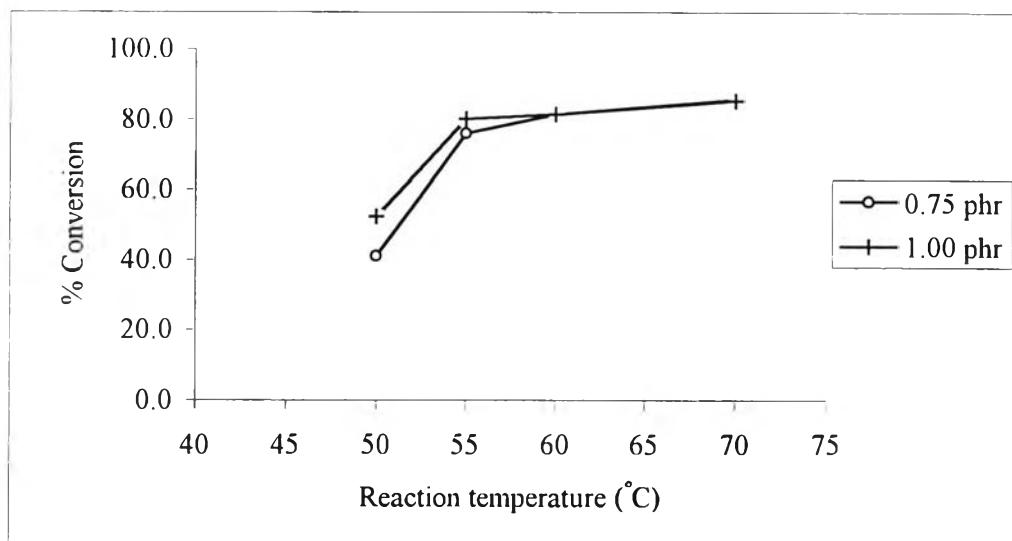


Figure 4.8 Effect of the reaction temperature on the percentage conversion; MMA 100 phr, $K_2S_2O_8$ 0.75-1.00 phr and time 8 hr.

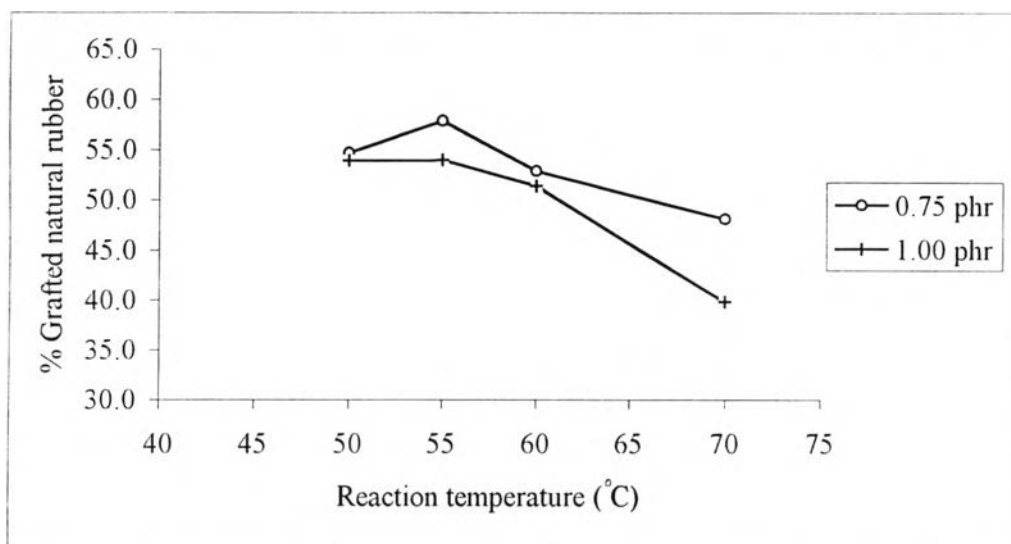


Figure 4.9 Effect of the reaction temperature on the percentage grafted natural rubber; MMA 100 phr, $K_2S_2O_8$ 0.75-1.00 phr and time 8 hr.

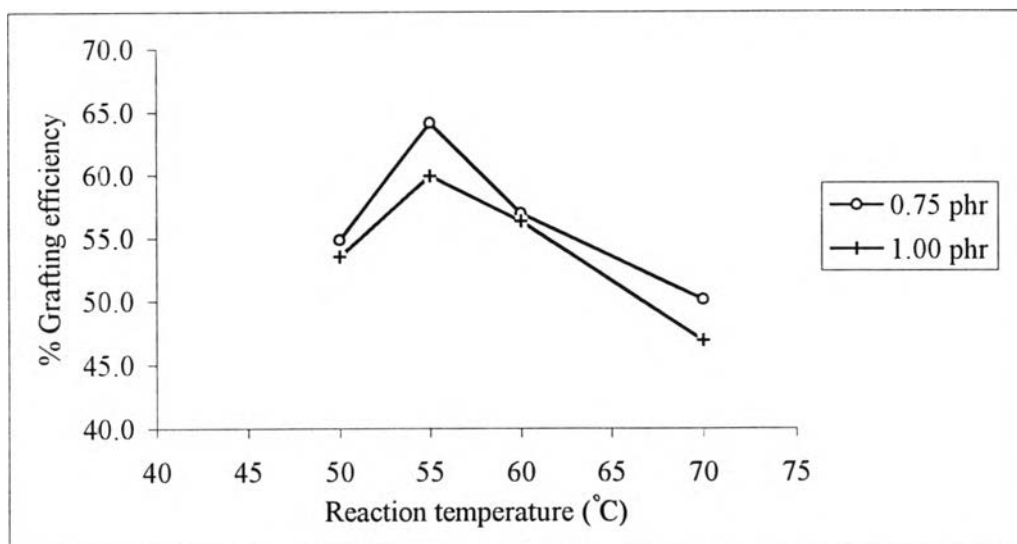


Figure 4.10 Effect of the reaction temperature on the percentage grafting efficiency; MMA 100 phr, $K_2S_2O_8$ 0.75-1.00 phr and time 8 hr.

4.2.3 Effect of Monomer Concentration

In this case, the natural rubber latex as used as backbone polymer of *cis*-1,4-polyisoprene, and methyl methacrylate monomer was added as a grafting monomer to polymerize with the polymer backbone. Natural rubber particles were swollen with the monomer, which was then polymerized onto natural rubber latex particles.

The effects of monomer concentration on the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency were investigated using the monomer concentration in the range of 0.50 - 2.00 phr and holding the other parameter constant. The details of all data and calculations are shown in Appendix A. The parameters of graft copolymerization were obtained as follows:

- Rubber content : 100 phr
- Monomer concentration : 40-120 phr
- Initiator concentration : 0.75 phr
- Reaction temperature : 55°C
- Reaction time : 8 hr.

Table 4.5 and Figure 4.11b show that the monomer concentration increases, percentage conversion also increases. In Figures 4.11a and 4.11b the percentage grafting efficiency and percentage grafted natural rubber reach maximum at monomer concentration of 100 phr, and thereafter it decreases. At higher monomer concentration, many reactions compete with grafting reaction probably take place in solution. Homopolymerization is more pronounced than grafting at higher monomer concentration. In addition, the increasing conversion may lead to thickening or hardening of the shell of latex particles.

4.2.4 Effect of Reaction Time

The effect of reaction time on the grafting of methyl methacrylate onto natural rubber is shown in Table 4.5 and Figures 4.12a - 4.12b. The details of all data and calculations are shown in Appendix A. The parameters of graft copolymerization were obtained as follows:

- Rubber content : 100 phr
- Monomer concentration : 100 phr
- Initiator concentration : 0.75 phr
- Reaction temperature : 55°C
- Reaction time : 4-10 hr.

From Figures 4.12a and 4.12b, it can be seen that as the reaction time increases, there is an increase in the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency in the lower reaction time range. At reaction time of 8 hr, it reaches a maximum value percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency, thereafter decreases slightly percentage of grafted natural rubber and grafting efficiency. It may be PMMA homopolymers are formed more readily than the graft copolymer.

Optimum condition for preparation of the grafted natural rubber was found as follows: the rubber content 100 phr, the initiator concentration 0.75 phr, the reaction temperature 55°C, the monomer concentration 100 phr, and the reaction time 8 hours. Which gave the grafting efficiency of 64.1%. The grafted natural rubber product has the grafting properties comparable to the grafted copolymer prepared by using cumene hydroperoxide and tetraethylenepentamine as initiator, that has grafting efficiency of 60% [3].

Table 4.5 Effect of the monomer concentration and reaction time on the percentage conversion, percentage grafting efficiency, and percentage grafted natural rubber; initiator concentration 0.75-1.00 phr and temperature 55°C.

	Monomer concentration, phr (8hr.)					Reaction time, hr (MMA 100 phr)			
	40	60	80	100	120	4	6	8	10
Conversion (%)	56.0	64.9	74.3	75.9	75.7	67.9	74.5	75.9	74.9
Grafting efficiency (%)	30.2	42.6	53.0	64.1	49.9	40.9	59.8	64.1	57.8
Graft properties									
Grafted natural rubber (%)	23.1	37.4	51.2	57.9	44.2	30.4	53.8	57.9	50.6
Free NR (%)	64.1	46.5	31.4	26.6	32.0	41.7	29.0	26.6	31.3
Free PMMA (%)	12.8	16.1	17.5	15.4	23.8	23.9	17.2	15.4	18.1

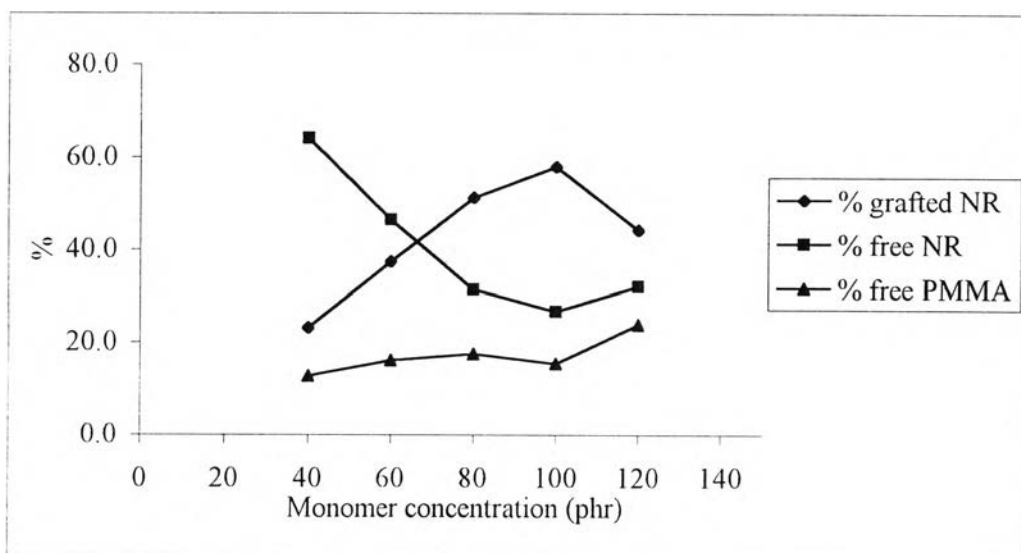


Figure 4.11a Effect of the monomer concentration on the percentage grafted natural rubber, percentage free NR, and percentage free PMMA; $K_2S_2O_8$ 0.75 phr, temperature 55°C , and time 8 hr.

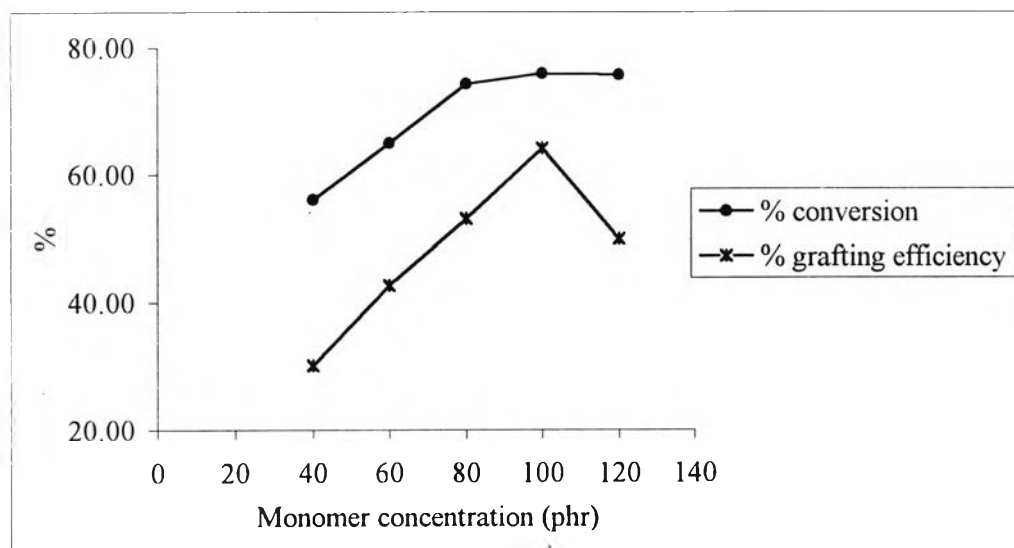


Figure 4.11b Effect of the monomer concentration on the percentage conversion and percentage grafting efficiency; $K_2S_2O_8$ 0.75 phr, temperature 55°C , and time 8 hr.

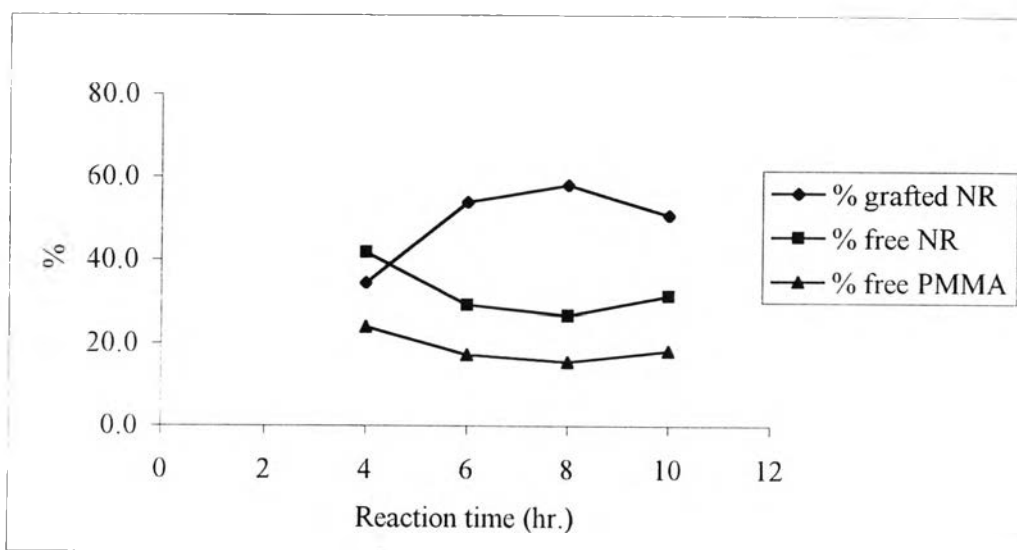


Figure 4.12a Effect of the reaction time on the percentage of grafted natural rubber, free NR, and free PMMA; MMA 100 phr, $K_2S_2O_8$ 0.75 phr, and temperature $55^\circ C$.

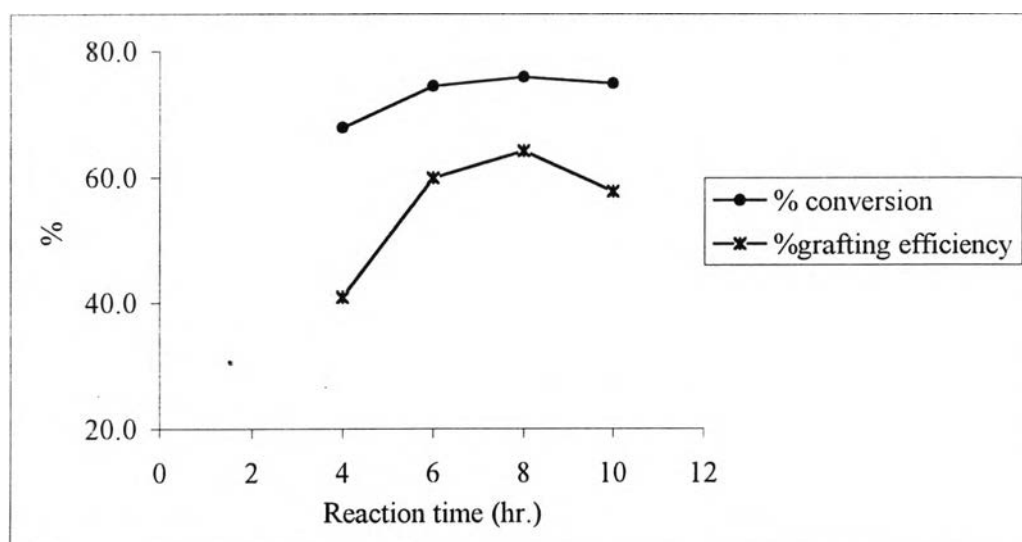


Figure 4.12b Effect of the reaction time on the percentage conversion and percentage grafting efficiency; MMA 100 phr, $K_2S_2O_8$ 0.75 phr, and temperature $55^\circ C$.

4.3 Characterization of Grafted Natural Rubber

4.3.1 Functional Groups in the Grafted Natural Rubber

The formation of natural rubber graft methyl methacrylate (NR-g-MMA) was confirmed by FT-IR measurement. Figures 4.13 and 4.14 show the infrared spectra in the region of 4000 – 400 cm^{-1} for natural rubber and grafted natural rubber. The assignments were given in Table 4.6. The FT-IR spectra of natural rubber exhibited the characteristic absorption bands of the C-H stretching vibration in aliphatic C-H bond at 1376 cm^{-1} , the C=C stretching vibration at 837 cm^{-1} and the C-C stretching vibration at 1243 cm^{-1} [37]. The new peaks in FT-IR spectrum of the grafted natural rubber show an intense absorption at 1733 and 1148 cm^{-1} corresponding to the C=O and C-O-C groups in the methacrylate chain along with the characteristic absorption of the NR group [3, 4]. This confirms the occurrence of grafting.

Table 4.6 The important characteristic peaks for the FT-IR spectra of the grafted natural rubber.

Natural rubber		NR-g-PMMA	
Wave number (cm^{-1})	Assignment	Wave number (cm^{-1})	Assignment
837	C=C stretching	837	C=C stretching
1243	C-C stretching	1148	C-O-C stretching
1376	C-H stretching	1243	C-C stretching
		1376	C-H stretching
		1733	C=O stretching

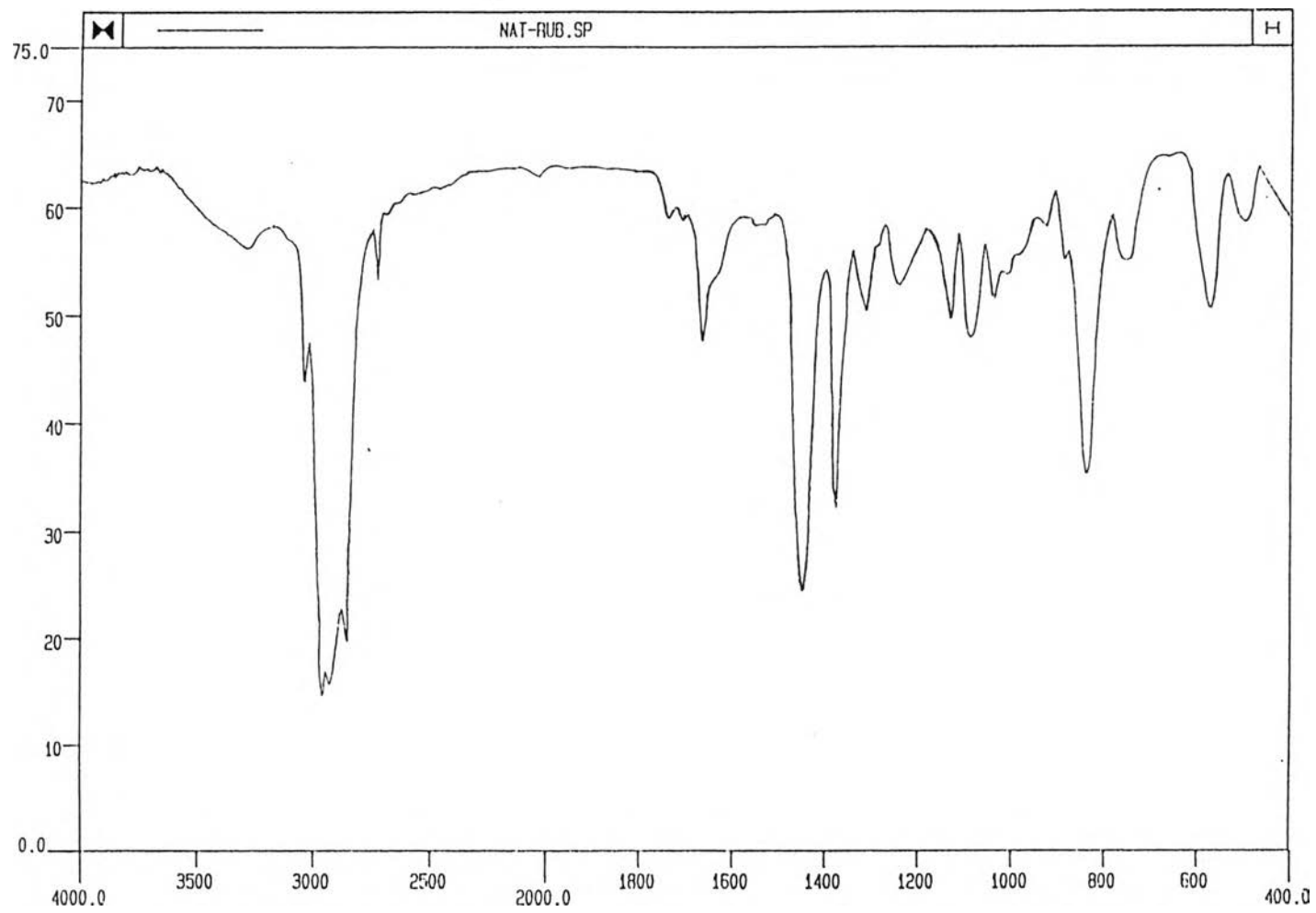


Figure 4.13 FT-IR spectrum of NR.

CM-1

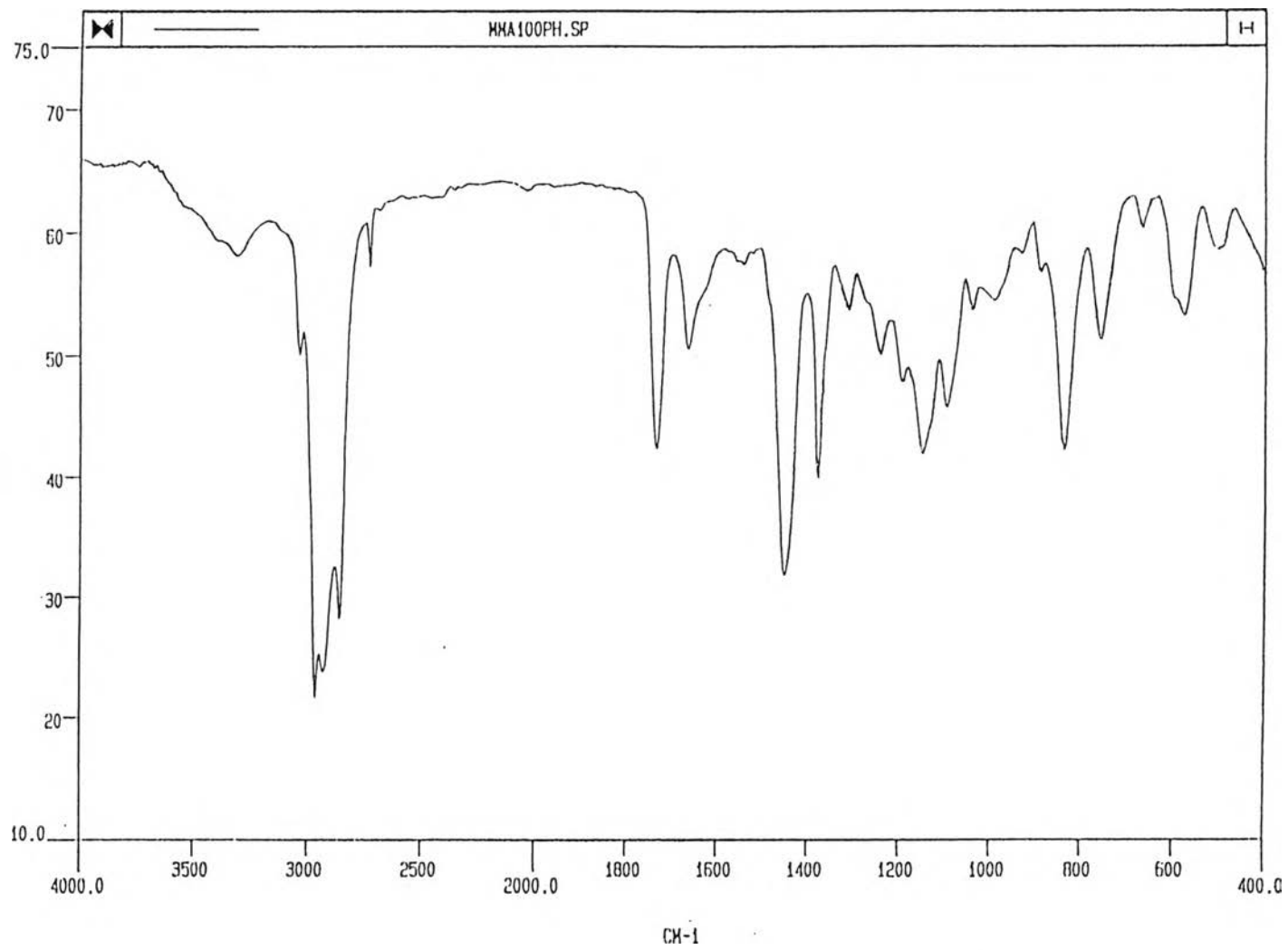


Figure 4.14 FT-IR spectrum of NR-g-MMA (MMA 100 phr).

4.3.2 Dynamic Mechanical Thermal Analysis (DMTA)

Transition phenomena were investigated with a dynamic mechanical thermal analysis. The temperatures at which damping ($\tan \delta$) peaks were observed are quoted as the transition temperatures. The dynamic mechanical properties of the grafted natural rubber at different monomer concentrations were measured at 1 Hz over the temperature range of -120 to $+110^\circ\text{C}$. The data for the grafted natural rubber are shown in Table 4.7 and Figure 4.15 - 4.17. The glass transition temperature (T_g) of NR was -72°C and pure PMMA was 105°C [7, 14].

Figure 4.17 shows the dependence of the storage modulus on temperature of grafted natural rubber by MMA 60, 80, 100, 120 phr. The storage modulus decreases with increasing temperature. This is due to the relaxations arising from local motions of the polymer chain, to be very extreme around the transition region. The storage modulus increases with increasing MMA concentration up to 100 phr and dropped at the higher concentration. The increase in storage modulus is expected as the MMA addition generally results in an increase of the stiffness of the grafted natural rubber, this contributed to the higher mechanical properties. The decrease in the storage modulus of grafted natural rubber observed, when MMA concentration was 120 phr because the packing of grafted natural rubber aggregated hard reached a critical point when they were no longer separated by the polymer materials [35].

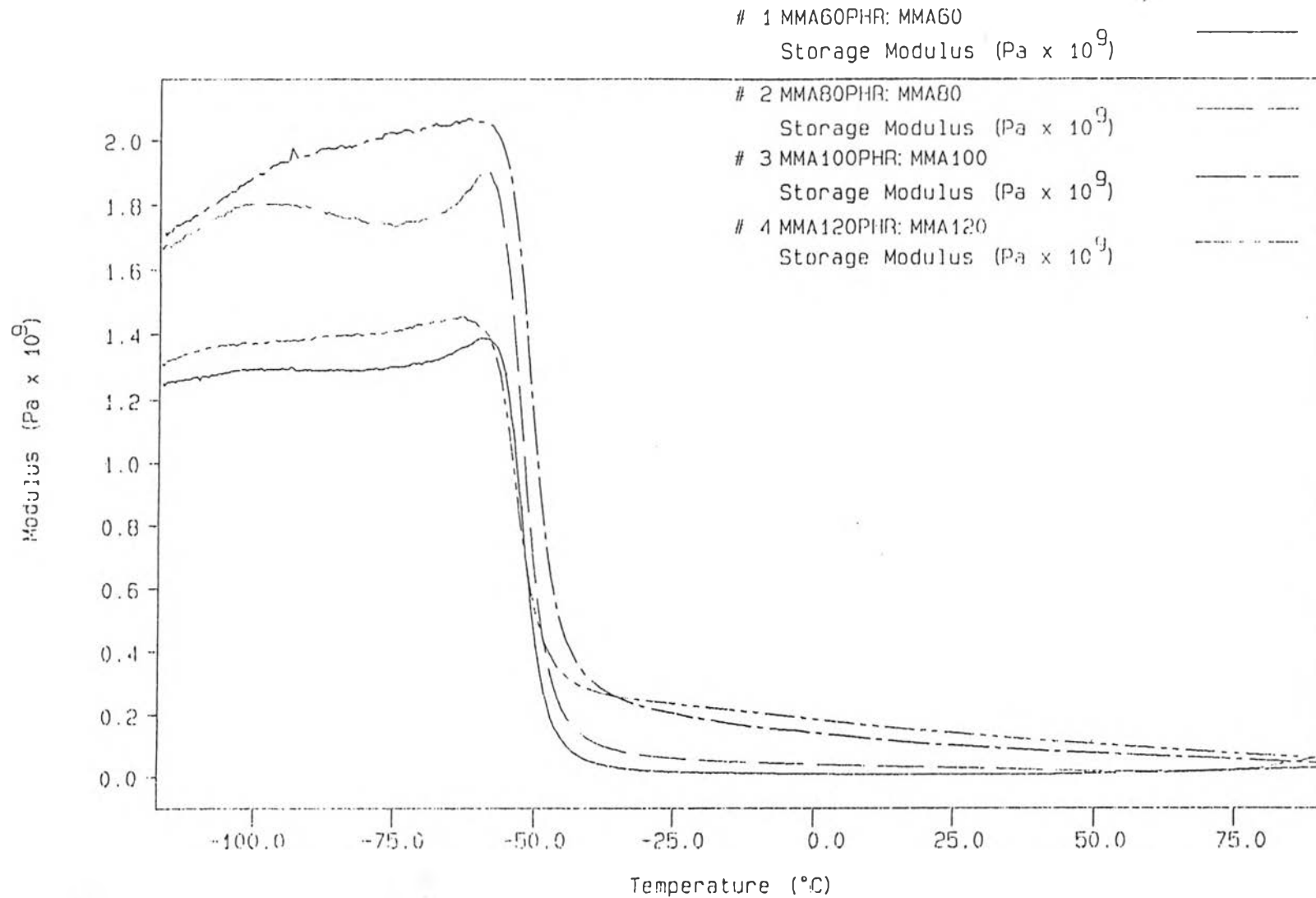
The effect of MMA concentration on the value of $\tan \delta$ is shown in Figure 4.16 and Table 4.7. It can be seen that $\tan \delta$ showed the maximum values around the transition region. It is apparent that the large energy loss peaks were associated with the large changes in the modulus. This may result from the high energy input used for joint motion of parts of the main polymer chains in the transition region. It was also found that $\tan \delta$ dropped as a consequence of MMA concentration. This shows the higher interaction between the NR and MMA of grafted natural rubber. The

overall width of the $\tan \delta$ peaks, it was found that the peaks became clearly broadened with the MMA concentration decreased. It indicated the greater dynamic losses. The losses could be due to more mechanical energy input converted to heat generated during the deformation and more energy losses in the movements of the polymer chain.

The variation of T_g of the grafted natural rubber at various MMA concentration is shown in Figures 4.16 - 4.18 and Table 4.7. The transition peak of grafted natural rubber changes proportionally with change of the MMA concentration. It can be seen that T_g of the grafted natural rubber was shown between the T_g of natural rubber and PMMA. The glass transition temperature and $\tan \delta$ of grafted natural rubber decreased with increasing MMA concentration.

Table 4.7 Glass transition temperature and $\tan \delta$ of the grafted natural rubber by DMTA technique.

Grafted natural rubber	T_g ($^{\circ}\text{C}$)	$\tan \delta$
Natural rubber	-72	-
MMA 60 phr	-45.62	0.858
MMA 80 phr	-47.07	0.677
MMA 100 phr	-47.02	0.508
MMA 120 phr	-50.14	0.387
PMMA	105	-



TEMPI: -120.0 C TIME: 0.0 min RATE: 10.0 C/min
 TEMPE: 110.0 C

Figure 4.15 Effect of MMA concentration on the storage modulus of grafted natural rubber.

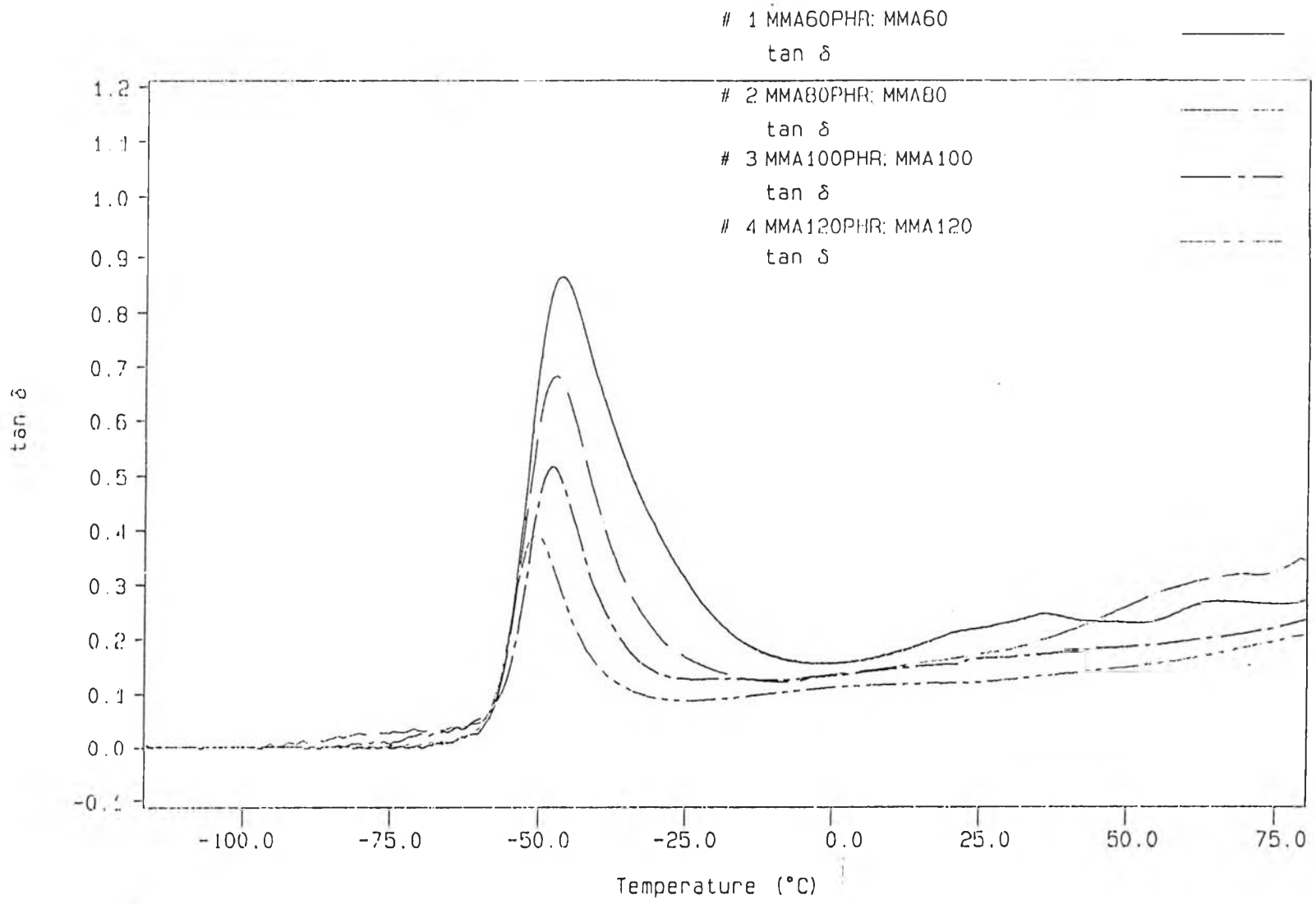
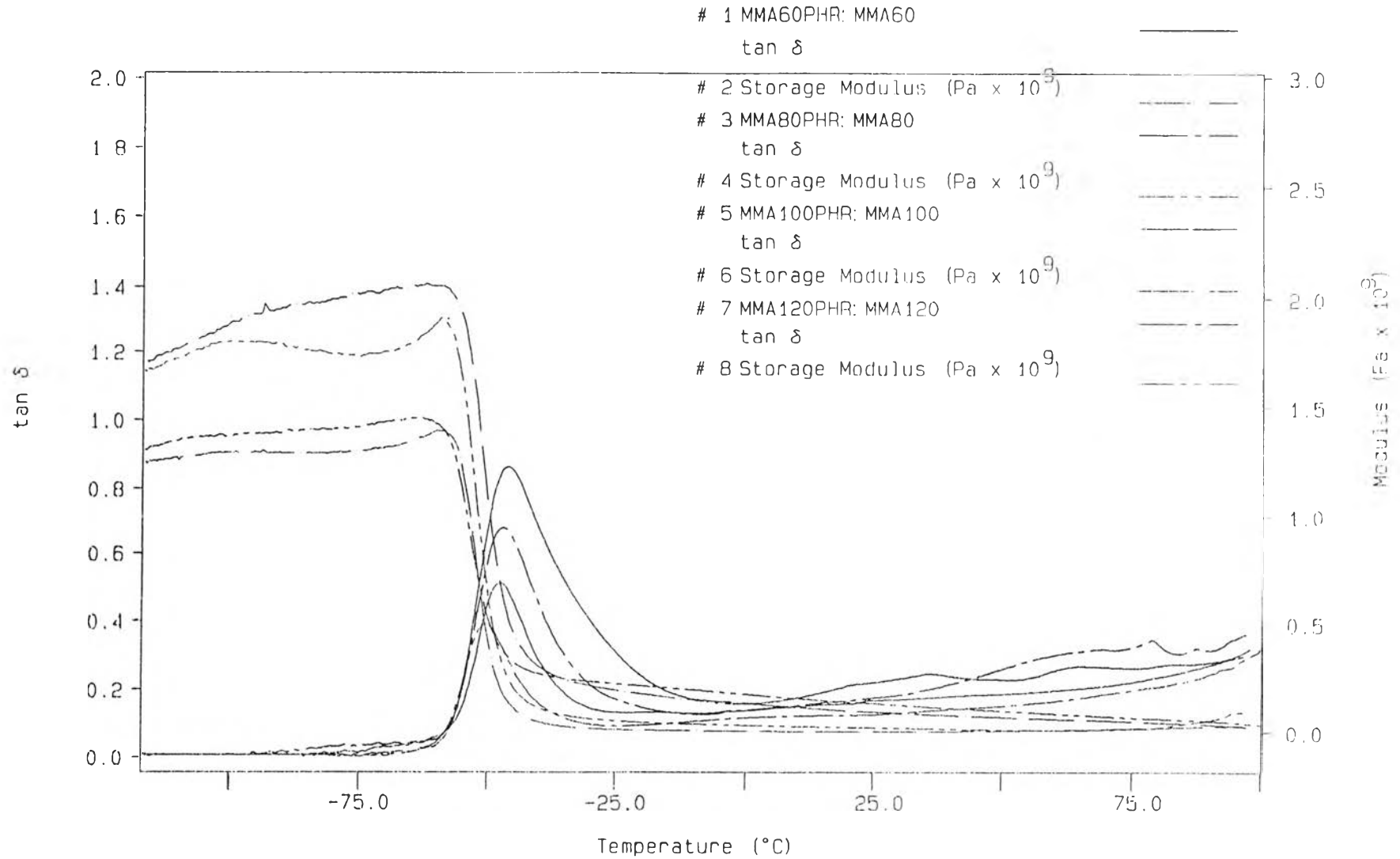


Figure 4.16 Effect of MMA concentration on the tan δ of grafted natural rubber.



TEMP1: -120.0 $^{\circ}$ C TIME1: 0.0 min RATE1: 10.0 $^{\circ}$ C/min
 TEMP2: 110.0 $^{\circ}$ C

Figure 4.17 Dynamic mechanical properties of grafted natural rubber (MMA 60-120 phr).

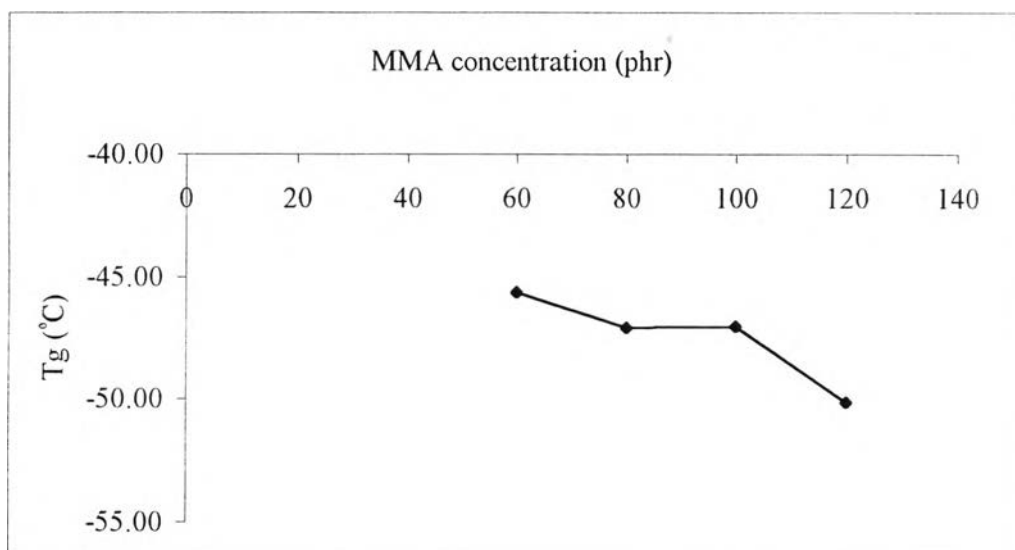


Figure 4.18 Effect of MMA concentration on T_g of grafted natural rubber.

4.3.3 Grafted Natural Rubber Morphology

In the graft copolymerization of natural rubber latex, the grafting reaction occurred largely on the surface of the rubber particles. This is true if the initiator used for the grafting reaction is water-soluble initiator [25]. In the work, potassium persulfate was used as water-soluble initiator. Radicals which are generated in the surface region of the particles cannot diffuse quickly due to the high viscosity within the natural rubber particles. At the surface, the radical concentration is considerably higher than in the center of the latex particle [36].

Figure 4.21 - 4.23 show TEM micrographs of grafted natural rubber latex particles by MMA 100 phr. The natural rubber seed latex shows mainly a spherical morphology of polymer particles with a thin PMMA film. It is possible that a thin layer of grafting PMMA covered natural rubber seed particles.

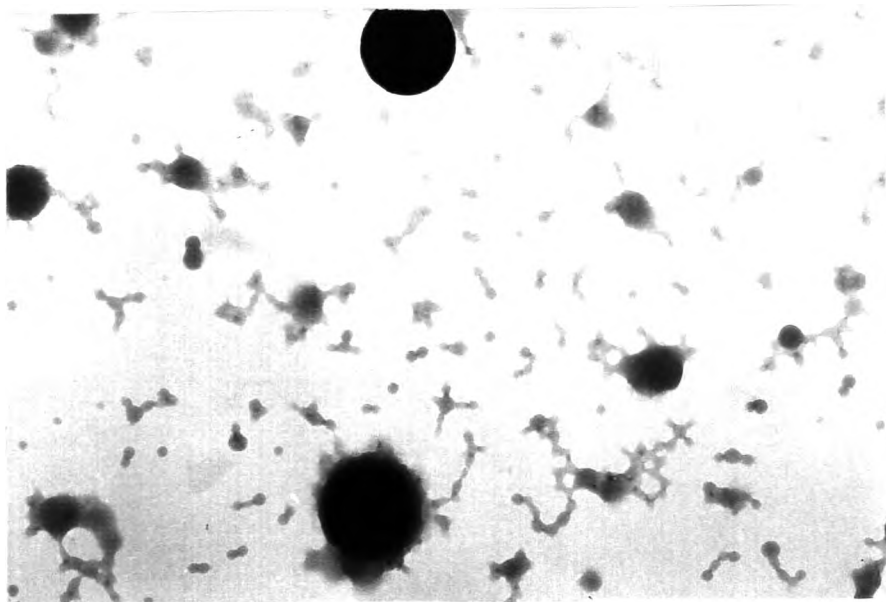


Figure 4.19 Transmission electron micrograph of the grafted natural rubber latex (MMA100 phr, X22,500).

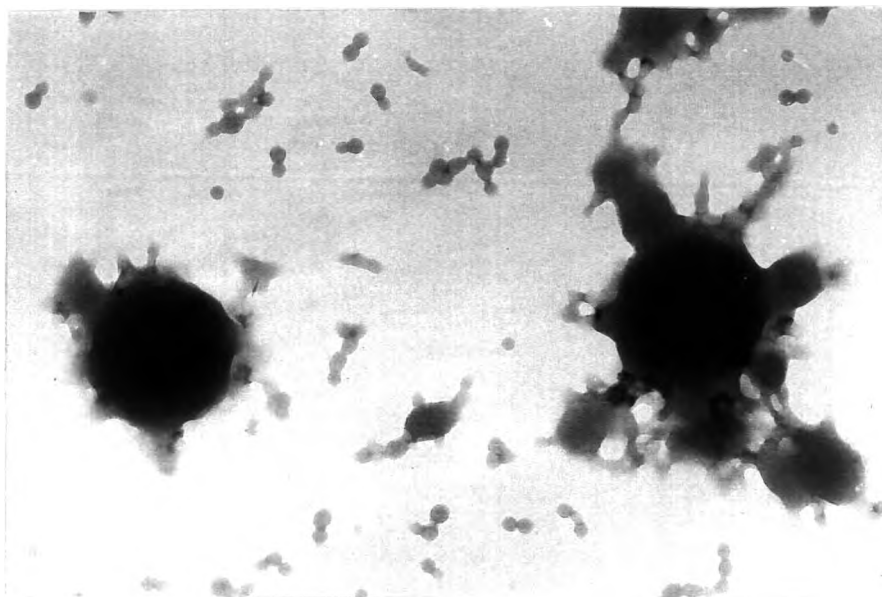


Figure 4.20 Transmission electron micrograph of the grafted natural rubber latex (MMA100 phr, X30,000).

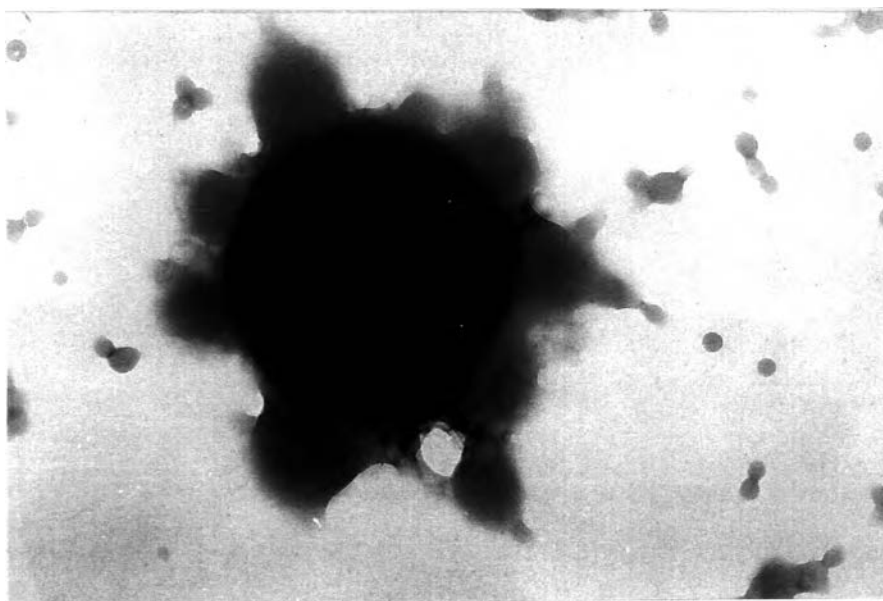


Figure 4.21 Transmission electron micrograph of the grafted natural rubber latex (MMA100 phr, X45,000).

4.4 Blending of Grafted Natural Rubber and PMMA

4.4.1 Properties of Grafted Natural Rubber Product

The hardness of grafted natural rubber product at various monomer concentrations are shown in Table 4.8 and Figure 4.22. The hardness of the grafted natural rubber product increased with increasing concentration of MMA. This suggests that the increased concentration of MMA may cause the increase of the hard segment given by PMMA grafted chain and PMMA homopolymer. The order of hardness follows the sequence:

$$\text{GNR120} > \text{GNR100} > \text{GNR 80} > \text{GNR60} > \text{GNR40}$$

Table 4.8 The hardness of grafted natural rubber product in different MMA concentration.

MMA concentration (phr)	Hardness (Shore D)
40	2.4
60	15.0
80	21.2
100	31.4
120	38.6

This grafted natural rubber will be used for applications which require a hard rubber with optimum retention of properties such as tensile properties and tear strength. In this research, the grafted natural rubbers with MMA 60 and 100 phr were selected for the preparation of thermoplastic elastomer.

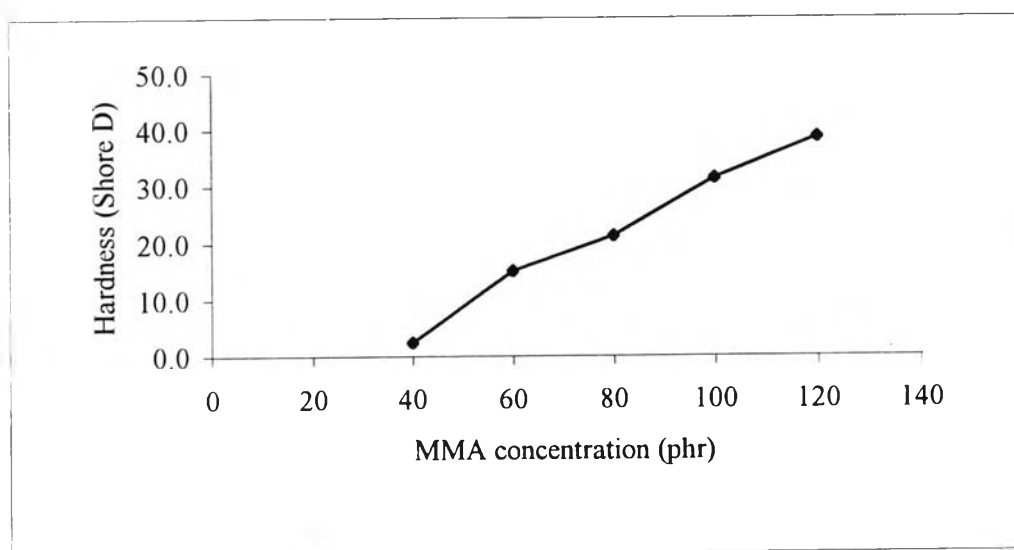


Figure 4.22 Effect of MMA concentration on hardness of grafted natural rubber.

The grafted natural rubber product was prepared by emulsion polymerization. The conditions were rubber content of 100 parts by weight, MMA of 60 or 100 phr, initiator of 0.75 phr. and the reaction temperature of 55°C for 8 hours. The grafting properties of grafted natural rubber products are also presented in Table 4.9.

Table 4.9 Grafting properties of grafted natural rubber.

	GNR60	GNR100
Conversion (%)	64.9	75.9
Grafting efficiency (%)	42.6	64.1
Graft Properties		
Grafted natural rubber (%)	37.4	57.9
Free NR (%)	46.5	26.6
Free PMMA (%)	16.5	15.4

4.4.2 Properties of PMMA

The typical data of PMMA (Crystallite MF#001) is shown in Table 4.10. The grafted natural rubber product prepared by emulsion polymerization has the grafting properties as shown in Table 4.8. The grafted natural rubber and PMMA blends were prepared and the mechanical properties of the blends were investigated.

Table 4.10 Typical data of PMMA (Crystallite MF#001)

Property	Value
Specific gravity	1.19
Water absorption, (%)	0.3
Thermal specific heat, (cal/g/°C)	0.35
Coefficient of linear thermal conductivity, (cm/cm/°C)	6×10^{-5}
Heat distortion temperature, (°C)	83

4.4.3 Mechanical Properties of Grafted Natural Rubber/PMMA Blends

The effects of the composition of grafted natural rubber/PMMA blends on the mechanical properties were investigated. The value of hardness, tensile properties and tear strength as shown in Table 4.11.

1. Hardness

The hardness of GNR60/PMMA and GNR100/PMMA blends are shown in Table 4.11 and Figure 4.23. From Figure 4.23, it can be seen that PMMA can enhance the hardness properties. The hardness increased with increasing PMMA component in GNR/PMMA blends. The hardness of GNR100/PMMA blends are higher than GNR60/PMMA blends for various content of PMMA. This is due to the hard segments of PMMA grafted chain in GNR100 which are higher than GNR60.

2. Tensile properties

- Stress at maximum load:

In Table 4.11 and Figure 4.24, the stress at maximum load of GNR60/PMMA and GNR100/PMMA blends increase as the PMMA content increases. For GNR100 the stress at maximum load was higher than GNR60 for all range of GNR/PMMA blends, due to the higher percentage grafted natural rubber in GNR100. Therefore the increase of the percentage grafted natural rubber, improve the strength of the GNR/PMMA blends.

- Strain at maximum load:

From Figure 4.25, the strain at maximum load of GNR/PMMA blends decreased when increasing PMMA content, due to the presence of PMMA component (the brittle thermoplastic, low strain at break). The strain at maximum load of GNR100 was less than GNR60 for all range of GNR/PMMA blends.

3. Tear strength

The tear strength as a function of MMA content for GNR60 is shown in Figure 4.26. For the GNR60/PMMA blends, the tear strength considerably increases with increasing content of PMMA. The increase of MMA content may cause the increase of the hard segment of MMA grafted chain and PMMA homopolymer.

The tear strength of GNR100/PMMA blends reached maximum at GNR/PMMA ratio of 70/30, it may be due to the existance of continuous phases, which would give rise to inferior tear strength.

Table 4.11 Properties of GNR/PMMA blends.

Property	GNR60/PMMA				GNR100/PMMA			
	100/00	70/30	60/40	50/50	100/00	70/30	60/40	50/50
Hardness, (Shore D)	15.0	21.6	35.8	47.8	31.4	49.8	56.1	60.9
Stress at max. load, (MPa)	3.5	4.1	5.3	8.1	5.1	6.9	11.5	21.3
Strain at max. load, (%)	410.1	105.7	21.7	20.4	90.8	81.2	19.3	6.5
Stress @ 100% modulus, (MPa)	1.7	4.1	-	-	-	-	-	-
Tear strength, (N/mm)	13.2	15.5	16.3	25.0	28.7	61.9	46.1	44.2

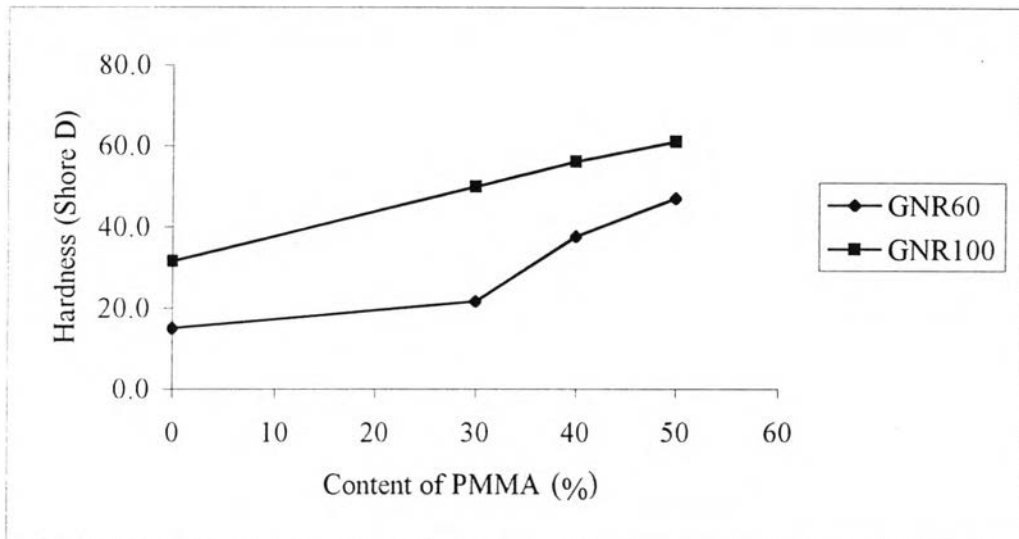


Figure 4.23 Effect of PMMA content in the GNR/PMMA blends on hardness.

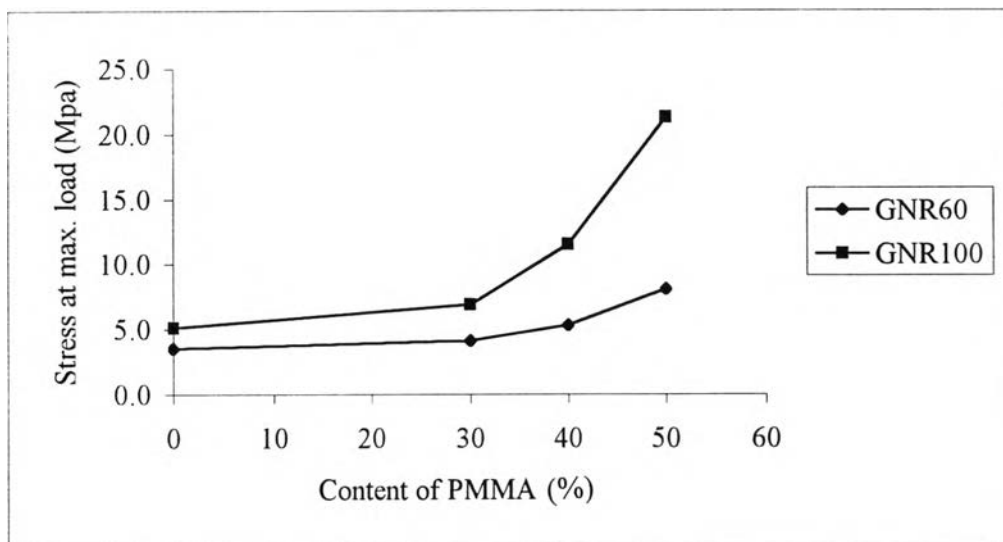


Figure 4.24 Effect of PMMA content in GNR/PMMA blends on stress at maximum load.

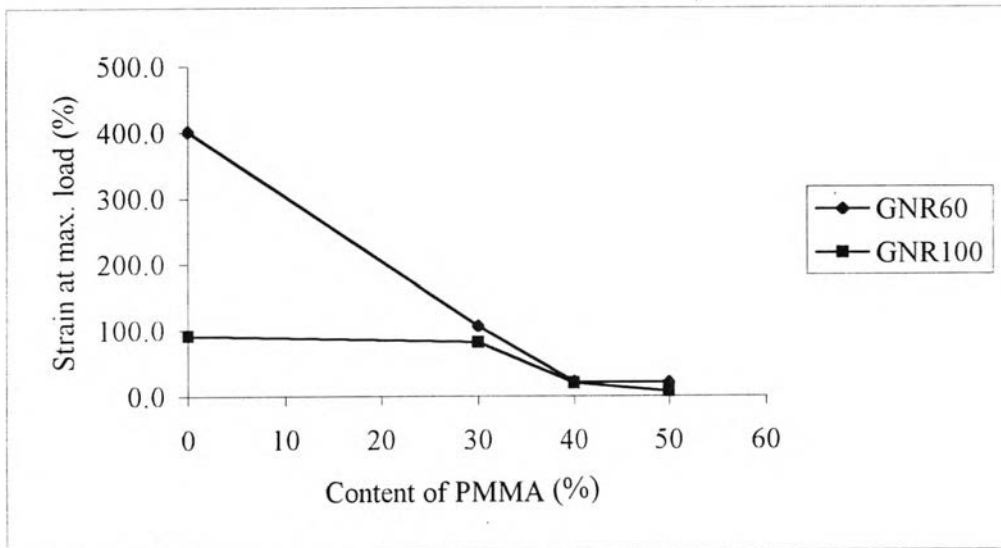


Figure 4.25 Effect of PMMA content in GNR/PMMA blends on strain at maximum load.

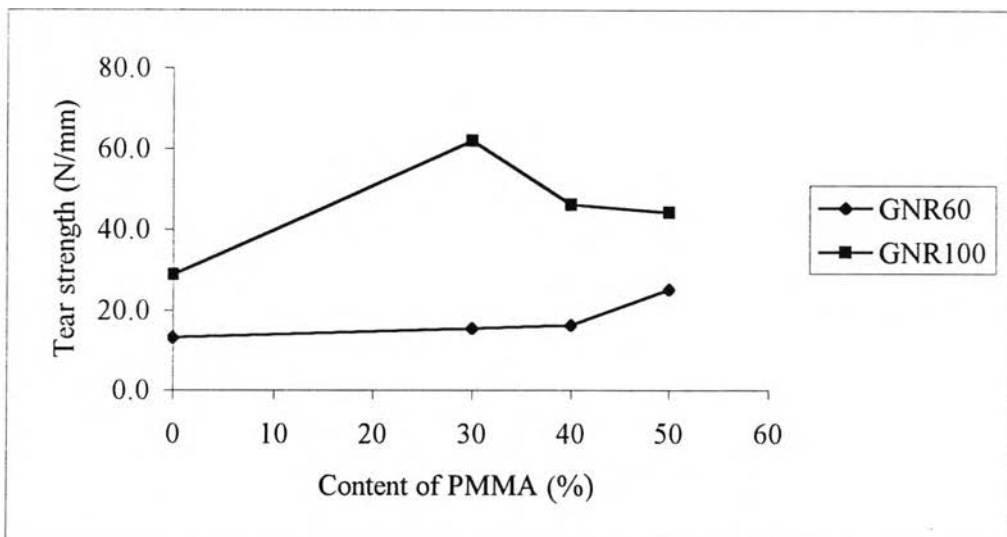


Figure 4.26 Effect of PMMA content in GNR/PMMA blends on tear strength.

4.4.4 Scanning Electron Microscopy (SEM)

The scanning electron microscope was employed to investigate the fracture surface of the specimen from the tensile properties test. Figure 4.27-4.29 show the surface of GNR60/PMMA blend at various ratio (X1500) and Figure 4.30-4.32 show the surface of GNR100/PMMA blend at various ratio (X1500). It can be seen that cavitation of the specimen decreased with increasing of PMMA content, the larger GNR content (70%) caused the increase cavitation sites. A cavity may form and grow, but the growth was interrupted by adjacent growing cavities formed by neighboring particles. For GNR100/PMMA blends the fracture surface were smoother than GNR60/PMMA blends at the same ratio of GNR and PMMA. Due to the better grafting properties of GNR100 than GNR60 (the higher percentage grafted natural rubber and percentage grafting efficiency), GNR100 blends had the better interfacial adhesion between the two phase of the blends than GNR60 blends. Therefore the increase of the percentage natural rubber and percentage grafting efficiency, improve the strength of the GNR/PMMA blends.

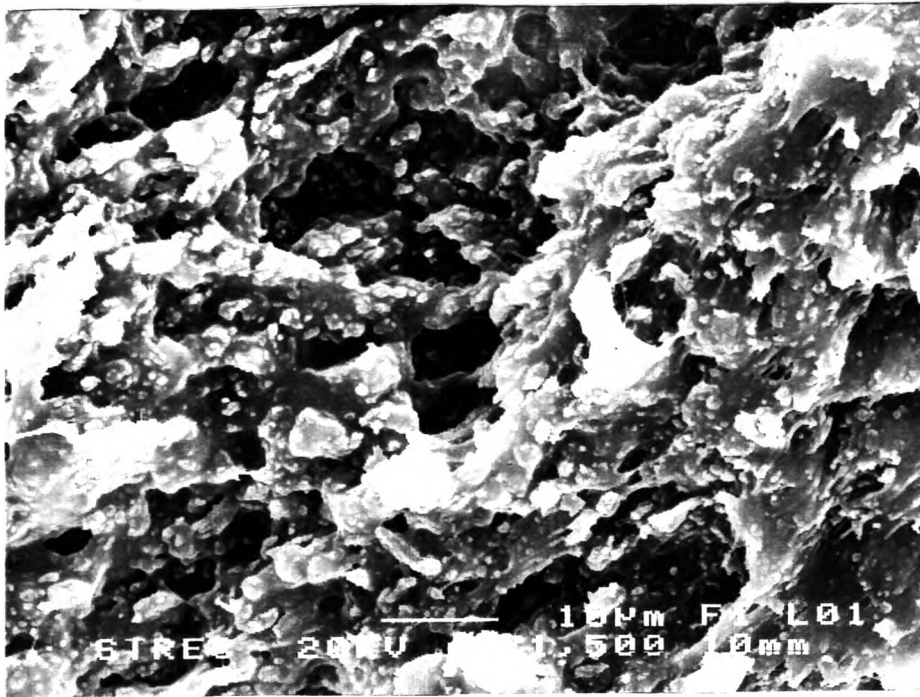


Figure 4.27 SEM photograph of GNR60/PMMA (70/30).

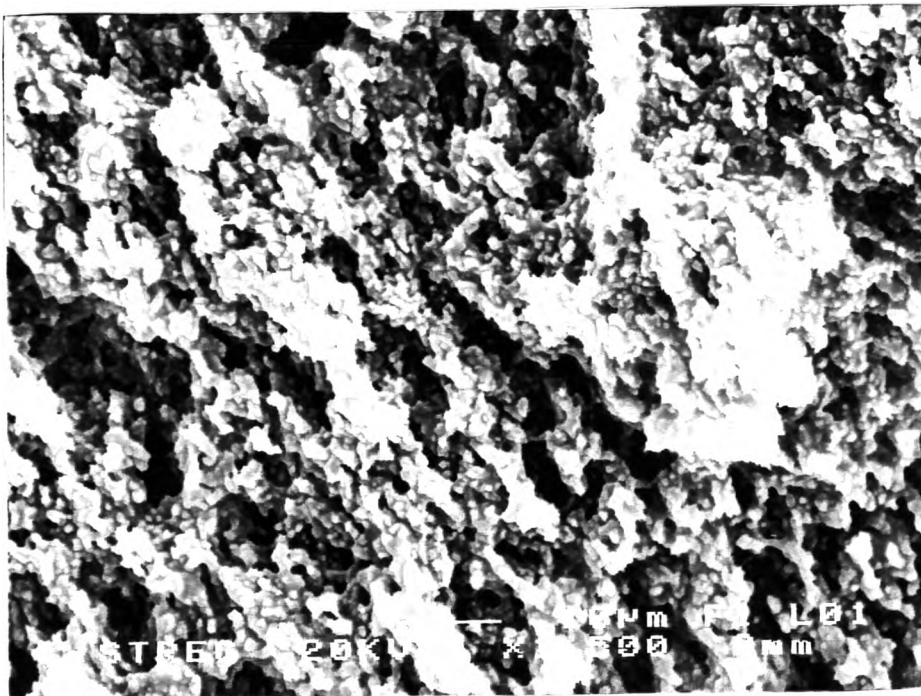


Figure 4.28 SEM photograph of GNR100/PMMA (70/30).

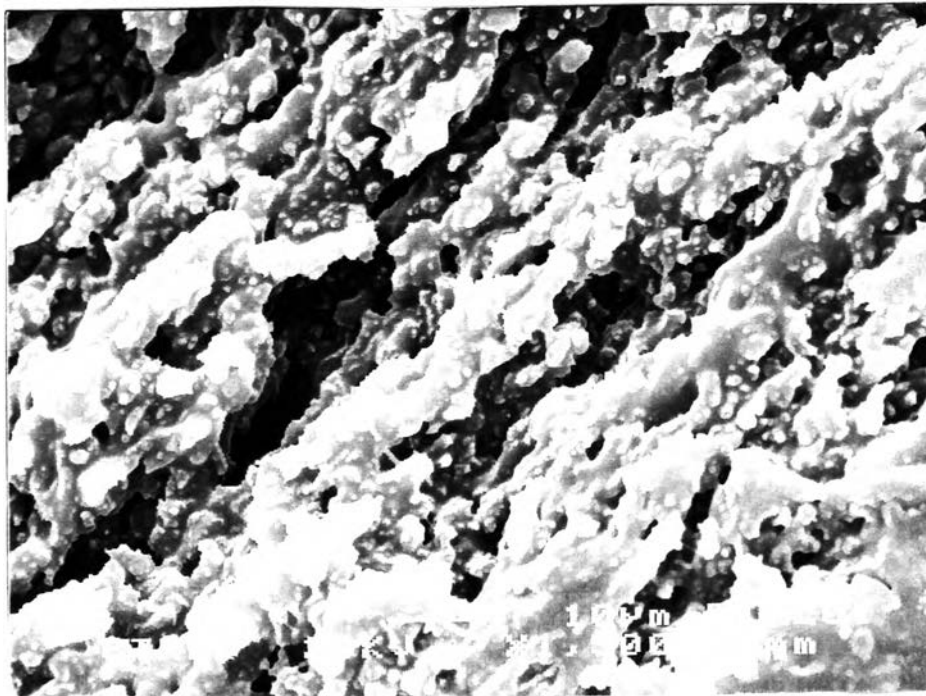


Figure 4.29 SEM photograph of GNR60/PMMA (60/40).

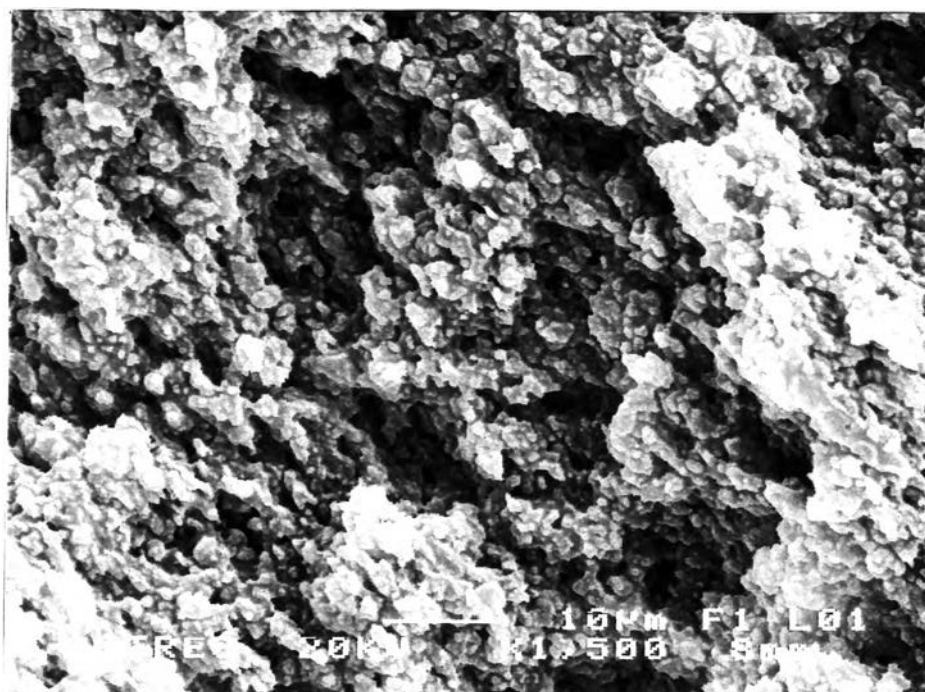


Figure 4.30 SEM photograph of GNR100/PMMA (60/40).



Figure 4.31 SEM photograph of GNR60/PMMA (50/50).

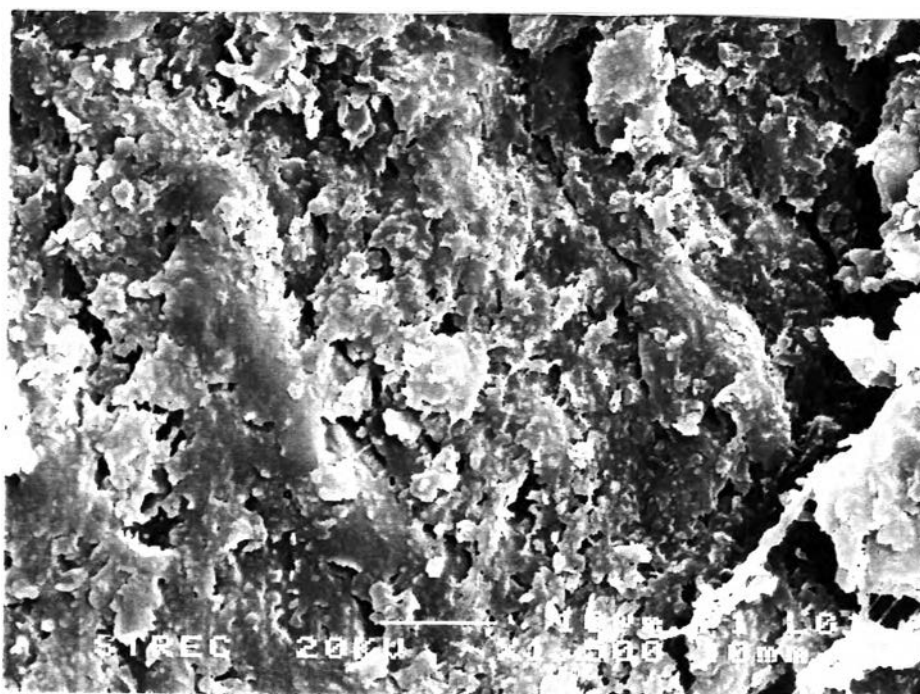


Figure 4.32 SEM photograph of GNR100/PMMA (50/50).