

CHAPTER IV

RESULTS AND DISCUSSION

In this study, the mechanical properties of the blends of grafted natural rubber and SAN resin was improved by increasing acrylonitrile and styrene ratio in graft copolymer. The grafted natural rubber was prepared by using the emulsion polymerization under various pressure and temperature.

The goal of this research is to obtain the optimum condition in emulsion polymerization of grafted natural rubber by varying the initiator concentration, reaction temperature and pressure. Then grafted natural rubber was blended with SAN resin to form the thermoplastics with various contents of grafted natural rubber. Finally, the mechanical properties of thermoplastics were investigated to find the optimum ratio of grafted natural rubber and SAN which give suitable properties.

4.1 Properties of Raw Materials

4.1.1 Natural Rubber Latex

The natural rubber latex consists of particles of rubber hydrocarbon and non-rubber constituents suspended in an aqueous serum phase. The average dry rubber content of latex may range between 60% and 61.0%

The properties of natural rubber latex, used in this study, is shown in Table 4.1. The molecular weight of natural rubber latex determined by GPC are as follows : $\bar{M}_n = 137,799$, $\bar{M}_w = 549,795$, $\bar{M}_z = 2,050,780$, $\bar{M}_w/\bar{M}_n = 3.99$. The particle size distribution of rubber particle was determined by the mastersizer as shown in Figure 4.1.

Table 4.1 The properties of natural rubber latex.

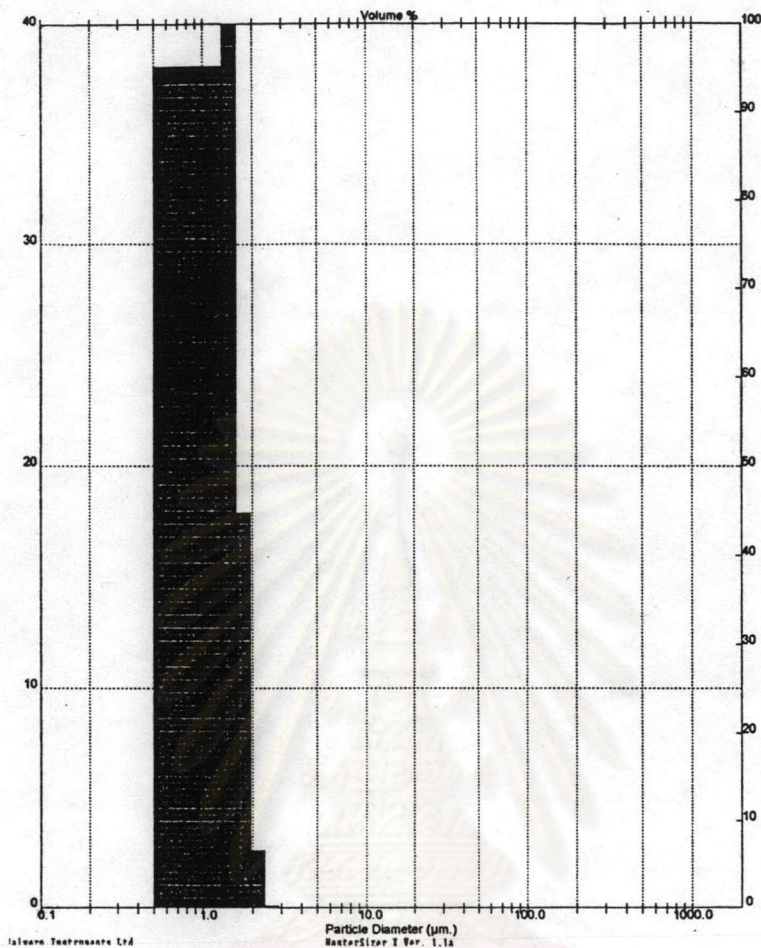
Type of latex : High Ammonia , Full Ammonia

Properties	Test results
Total Solids Content, %	61.96
Dry Rubber Content	60.09
Non Rubber Content	1.87
Ammonia Content (on Total Weight), %	0.76
Ammonia Content (on Water Phase), %	2.00
pH Value	10.75
KOH Number	0.5947
Volatile Fatty Acid Number (VFA)	0.0229
Mechanical Stability Time @ 55% TS.,Sec.	
On 12/02/96	970
Specific Gravity at 25 °C	0.945
Magnesium Content. (ppm.)	15
CST. (ml.)	2.8

Source : Thai Rubber Latex Corporation (Thailand Public Company Limited)

Bangplee Samutprakarn.

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Presentation: (ZOH) 1.330, 1.530 + 1 0.10000
Polydisperse model

Residual = 2.627 %	Concentration = 0.005 %	Focus = 300 mm.
d (0.5) = 1.38 µm	d (0.1) = 1.08 µm	Obscuration = 24.63 %
D [4, 3] = 1.29 µm	Span = 0.51	d (0.9) = 1.77 µm
Gaussian Mean (D[3,2]) = 1.15 µm		Mode = 1.41 µm
Specific Surface Area = 5.1907 sq. m. / gm		Density = 1.00 gm. / c.c.

Size (Lo) µm	Result in %	Size (Hi) µm	Result Below %	Size (Lo) µm	Result in %	Size (Hi) µm	Result Below %
0.50	38.18	1.32	38.18	25.48	0.00	31.01	100.00
1.32	40.92	1.80	79.09	31.01	0.00	37.79	100.00
1.80	18.10	1.95	97.19	37.79	0.00	46.03	100.00
1.95	2.71	2.38	99.90	46.03	0.00	58.09	100.00
2.38	0.10	2.90	100.00	58.09	0.00	68.33	100.00
2.90	0.00	3.53	100.00	68.33	0.00	83.28	100.00
3.53	0.00	4.30	100.00	83.28	0.00	101.44	100.00
4.30	0.00	5.24	100.00	101.44	0.00	123.59	100.00
5.24	0.00	6.39	100.00	123.59	0.00	150.57	100.00
6.39	0.00	7.78	100.00	150.57	0.00	183.44	100.00
7.78	0.00	9.48	100.00	183.44	0.00	223.51	100.00
9.48	0.00	11.55	100.00	223.51	0.00	272.31	100.00
11.55	0.00	14.08	100.00	272.31	0.00	331.77	100.00
14.08	0.00	17.15	100.00	331.77	0.00	404.21	100.00
17.15	0.00	20.90	100.00	404.21	0.00	492.47	100.00
20.90	0.00	25.48	100.00	492.47	0.00	600.00	100.00

Figure 4.1 Chart diagram showing the size distribution of rubber particles..

Specific surface area : 5.1997 sq.m./gm

Diameter : 1.06 µm

4.2 Preparation of Grafted Natural Rubber

The grafted natural rubber was prepared by graft emulsion polymerization. In this experiment, using sodium laurylsulfate and potassium persulfate as emulsifier and initiator respectively, various parameters which affected on the properties of grafted natural rubber, are emulsifier concentration, initiator concentration, monomer content, reaction temperature and pressure.

Rujinirun, C., [25], studied the effect of emulsifier concentration, monomer content and temperature conditions on the characteristics of grafted natural rubber. The appropriate conditions of graft copolymerization were obtained as follows :

- emulsifier concentration	1.5 parts by weight
- rubber content	100 parts by weight
- monomer content	100 parts by weight
- ratio of acrylonitrile and styrene	40:60
- reaction temperature	50 °C

In this work, the rubber and monomer contents were both 100 parts by weight and the ratio of acrylonitrile and styrene was 40:60. The emulsifier concentration was 1.5 parts by weight. The effect of initiator concentration, temperature and pressure on emulsion polymerization of grafted natural rubber were studied the appropriate condition, which yielded high percent conversion, grafting efficiency and acrylonitrile content in graft copolymer, for the preparation of graft copolymer of acrylonitrile and styrene onto natural rubber, were investigated.

4.2.1) Effect of initiator concentration

4.2.2) Effect of reaction temperature and pressure

4.2.1. Effect of Initiator Concentration

The effects of initiator concentration on the properties of grafted natural rubber were studied by varying the initiator concentration of 0.5, 1.0, 1.5, and 2.0 parts by weight (per 100 parts of total monomers). The amount of styrene and acrylonitrile monomer (60:40), reaction temperature and emulsifier concentration were kept constant, as follows :

- amount of styrene and acrylonitrile monomers : 100 parts by weight
- reaction temperature : 50 °C
- emulsifier concentration 1.5 parts by weight
- rubber content 100 parts by weight

In this study , the effect of initiator concentration on the graft characteristics were investigated. The graft characteristics of grafted natural rubber reported are degree of monomers conversion, grafting efficiency, graft ratio, free SAN chain length and graft frequency.

The monomers conversion is defined as the mass of SAN formed (grafted and free) divided by the mass of monomers. The grafting efficiency is readily defined as the mass of the grafted SAN divided by the total mass of grafted latex produced. The graft ratio is calculated from the total mass of styrene and acrylonitrile monomers which grafted on the backbone polymer divided by the mass of rubber which formed graft with styrene and acrylonitrile monomers. The graft frequency is the number of repeating unit between graft points. So, the graft frequency is computed by knowing the total numbers repeating units of graft chains and backbone chains, both derived from the molecular weight analysis by GPC. The detail of the calculations are shown in the Appendix A.

The monomers conversion, grafting efficiency and graft ratio of grafted natural rubber at various initiator concentration are shown in Table 4.2 and Figure 4.2 and 4.3. The detail of all data and calculations are shown in Appendix A.

According to the assumption, the graft chain lengths are on average equal to the free polymer chain lengths, therefore molecular weights of the free SAN and

grafted SAN are assumed to be the same. The chain length or molecular weight of polymer is inversely dependent on the initiator concentration or radical concentration. Increasing initiator concentration or radical polymerization leads to small-sized polymer molecules or low molecular weight. The effect of initiator concentration on molecular weight of free SAN is shown in Table 4.2 and Figure 4.4. The data are shown in the Appendix B.

The graft frequency is the number of repeating units between graft points. The effect of initiator concentration on the graft frequency is shown in Table 4.2 and Figure 4.5. The detail of all data and calculations are shown in Appendix A.

From Figure 4.2 and 4.3, the variation of initiator concentration affected the monomers conversion, grafting efficiency and graft ratio. The monomers conversion increased with increasing the initiator concentration. But above 1.5 parts by weight of initiator, monomers conversion and graft ratio increased slightly. The maximum grafting efficiency was 38.3 % at 1.5 parts by weight of initiator.

As can be seen in Figure 4.4, the molecular weight of free SAN decreased with increasing the initiator concentration. It can be explained that the increasing initiator concentration leads to the increasing radicals that can initiate the polymerization and the increase of radical concentration leads to low molecular weight of free SAN.

From Figure 4.5, the increasing initiator concentration led to decrease of the number of backbone polymer repeating units between graft chains or graft frequency because the free radical concentration increased. Therefore, the repeating units between grafted chains decreased with increasing the initiator concentration.

From Table 4.2, monomer conversion, grafting efficiency and graft ratio increased with increasing the initiator concentration and the graft frequency decreased with increasing the initiator concentration. At initiator concentration above 1.5 parts per weight gave the grafted natural rubber with desired grafting properties. The appropriate initiator concentration of 1.5 parts by weight was used.

Table 4.2 Effect of initiator concentration on the degree of monomers conversion and graft properties of grafted natural rubber : monomer : latex = 1:1;
temp. = 50 °C; pressure = 1 atm; time = 8 hrs.

Grafting Properties	Parts by weight of initiator			
	0.5	1.0	1.5	2.0
Grafted natural rubber (%)	50.6	51.6	52.4	51.4
Free SAN (%)	19.3	25.1	27.1	27.7
Free Natural rubber (%)	30.2	23.3	20.5	20.9
Conversion (%)	32.5	49.5	60.5	63.6
Grafting efficiency (%)	26.6	31.1	38.3	39.5
Graft ratio (g.g ⁻¹)	0.11	0.18	0.25	0.27
MW of free SAN				
\bar{M}_n	55,310	48,978	46,716	43,020
\bar{M}_w	364,028	354,740	264,989	237,487
\bar{M}_z	3,529,887	4,073,031	3,434,677	3,625,808
\bar{M}_w/\bar{M}_n	6.58	7.24	5.67	5.52
Graft Frequency	16,888	8,106	5,477	4,222

*graft copolymerization was carried in 4-Necked bottom reactor.

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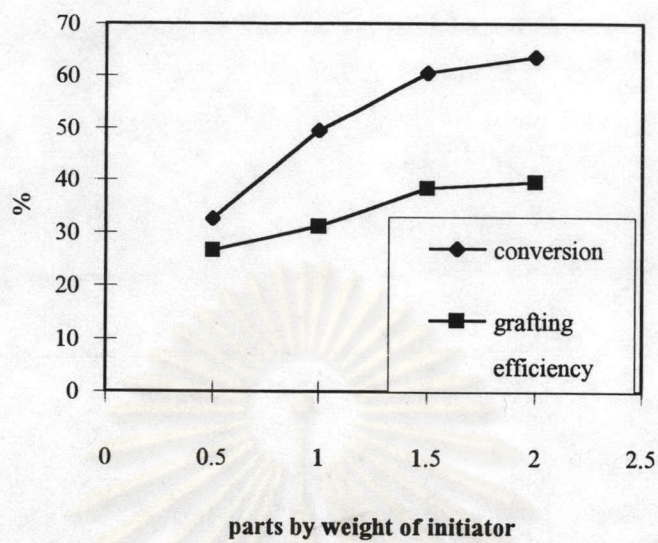


Figure 4.2 Effect of initiator concentration on monomers conversion and grafting efficiency.

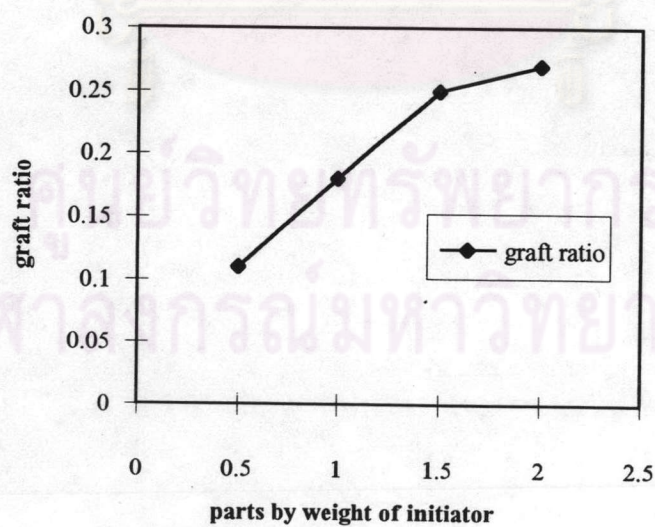


Figure 4.3 Effect of initiator concentration on the graft ratio.

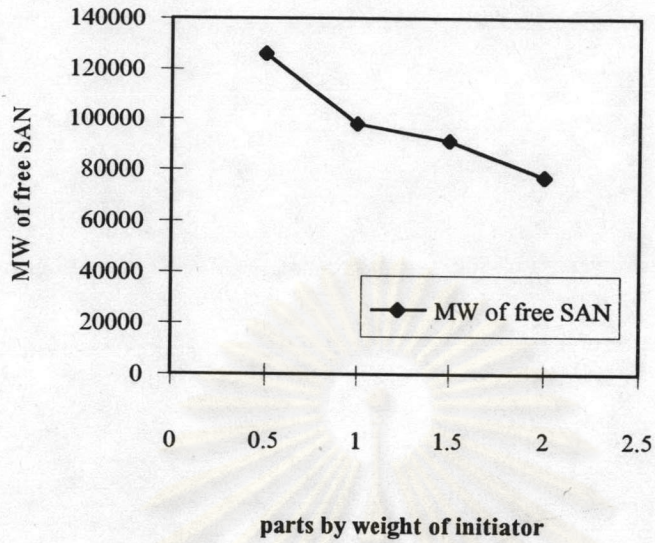


Figure 4.4 Effect of initiator concentration on the molecular weight of free SAN.

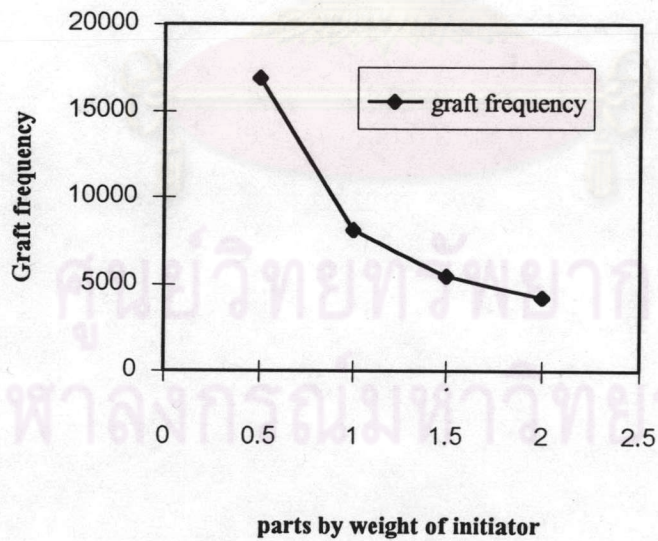


Figure 4.5 Effect of initiator concentration on the number of backbone polymer repeating units between graft chains (graft frequency).

4.2.2 Morphology of Grafted Natural Rubber

The preparation of grafted natural rubber was performed by emulsion polymerization process. In this case, the latex natural rubber were as an seed latex of *cis*-1,4-polyisoprene which as the isoprene monomer were polymerized first, and acrylonitrile monomer and styrene monomer subsequently added to continue polymerization within the seed particle. The key process lied in the grafting of a significant portion of the growing acrylonitrile styrene random copolymer radicals onto the double bonds of the existing elastomeric components. The grafting between the plastic and elastimer components led compatibility of the system, resulting in a favorable state of dispersion and also bonded the phases together. Upon the polymerization, the second monomer mixed with phase separation to yield the complex inner morphology. Small emulsion-grafted small particles exhibited a closed shell of graft copolymer on their surface, and no inclusion was visible in the images either before or after the mixing process.

The result indicated that the complete closed shell formed at 1.5 parts by weight of initiator. A scanning electron micrograph is shown in Figure 4.6 for the grafted natural rubber. The particles shown a regular spherical morphology. A transmission electron micrograph of grafted natural rubber is seen in Figure 4.7 and 4.8. The styrene-acrylonitrile copolymer layer on the outside of the particle by osmium tetroxide staining and interior structure, natural rubber, in the particle can also be seen.

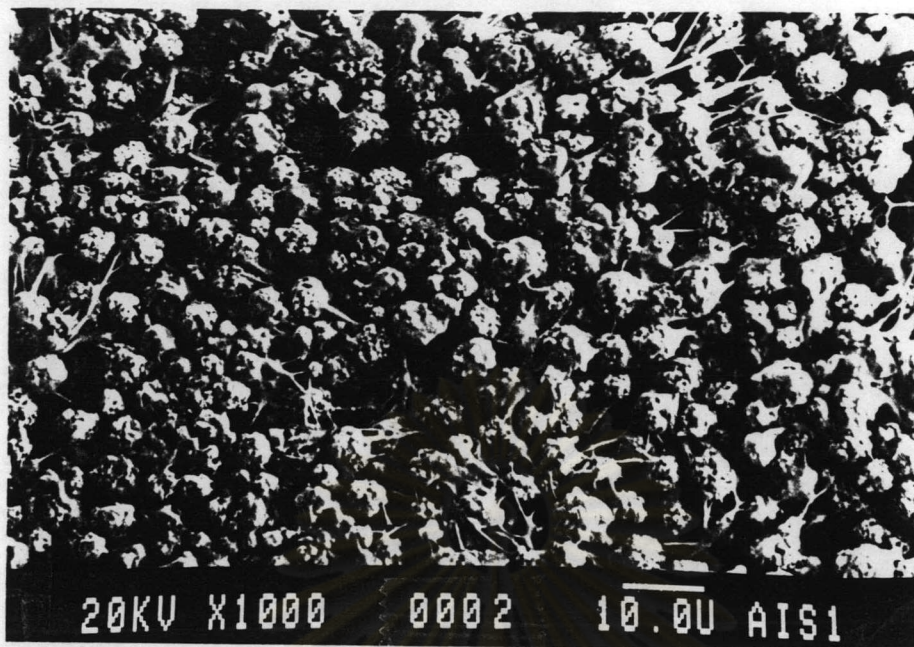


Figure 4.6 Scanning electron micrograph of coagulated particles from emulsion polymerization of grafted natural rubber latex.



Figure 4.7 Transmission electron micrograph of grafted natural latex particles
Mag 45,000X.

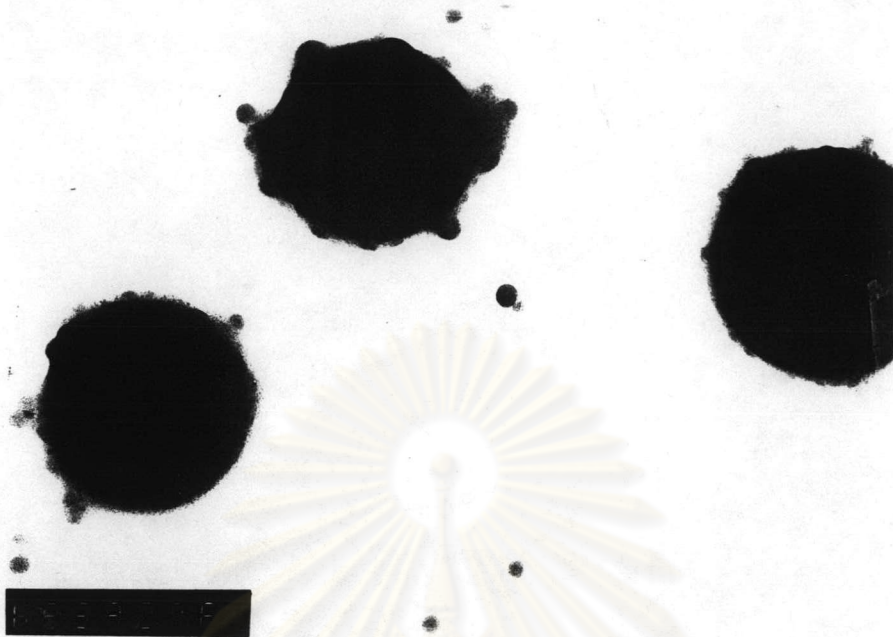


Figure 4.8 Transmission electron micrograph of grafted natural rubber latex
Mag 30,000X

4.2.3 Effect of Reaction Temperature and Pressure

The reaction temperature had a strong effect on the grafted natural rubber product, because the reaction temperature affected the reactivity ratio of monomers and ratio of acrylonitrile and styrene monomer in aqueous phase. Rujinirun, Chalampol [25] studied the effect of reaction temperature on the ratio of styrene and acrylonitrile in the grafted natural rubber. The styrene content increased with increasing the reaction temperature. The acrylonitrile content also slightly increased with increasing the reaction temperature from 30 to 50 °C. At the reaction temperature above 50 °C, the acrylonitrile content decreased but monomers conversion increased. The reason is that acrylonitrile monomer has low normal boiling point (77 °C), it vaporizes easily, thus the acrylonitrile content in aqueous phase decreases with increase temperature.

In this study graft copolymerization was carried out under pressure and temperature at above 50 °C, the increase of pressure caused the increase of

acrylonitrile content in aqueous phase. The effect of reaction temperature and pressure on the preparation of grafted natural rubber were investigated by varying the reaction temperature of 50, 60, 70 and 80 °C and varying pressure of 20, 40 and 60 psig. The effect of temperature and pressure on the graft characteristics, the copolymer composition and the thermal properties of grafted natural rubber were investigated.

The grafted natural rubber was prepared in emulsion polymerization for 8 hours using the following basic formulation :

Rubber content	100 parts by weight
AS monomer content	100 parts by weight
Ratio of acrylonitrile and styrene	40 : 60
Emulsifier	1.5 parts by weight
Initiator	1.5 parts by weight

4.2.3.1 Effect of Reaction Temperature and Pressure on Graft Efficiency and Graft Ratio

The effect of reaction temperature and pressure on monomers conversion, grafting efficiency and graft ratio are shown in Table 4.3. The detail of all data and calculation are presented in Appendix A.

From the Figure 4.9, 4.10 and 4.11 the monomers conversion, grafting efficiency and graft ratio increased with increasing temperature for each pressure. At the reaction temperature above 70 °C, the grafting efficiency and graft ratio decreased. With increasing temperature. At each pressure of 20 and 40 psig, the grafting efficiency and graft ratio were the same and maximum at 70 °C.

At pressure of 60 psig and the temperature range of 50-80 °C, the latex was coagulated before the stop of reaction. Thus, the pressure above 40 psig was not suitable condition for the preparation of graft natural rubber by emulsion polymerization because of the decrease of stability of latex.

Table 4.3 Effect of reaction temperature and pressure on degree of monomers conversion, grafting efficiency and graft ratio :
 monomer : latex = 1:1; initiator = 1.5 parts by weight; time = 8 hrs.

Pressure. (psig)	Temp. (°C)	% conversion	% grafting efficiency	graft ratio
0	50	60.6	33.9	0.31
20	50	63.7	34.7	0.34
	60	71.0	36.6	0.36
	70	85.3	42.1	0.45
	80	88.9	38.9	0.35
40	50	65.6	35.2	0.34
	60	79.7	39.7	0.40
	70	88.2	43.9	0.46
	80	92.7	36.2	0.34
60	50	- ^a	-	-
	60	-	-	-
	70	-	-	-
	80	-	-	-

^a : The latex was coagulated before stopping reaction

* graft copolymerization was carried in stainless steel reactor.

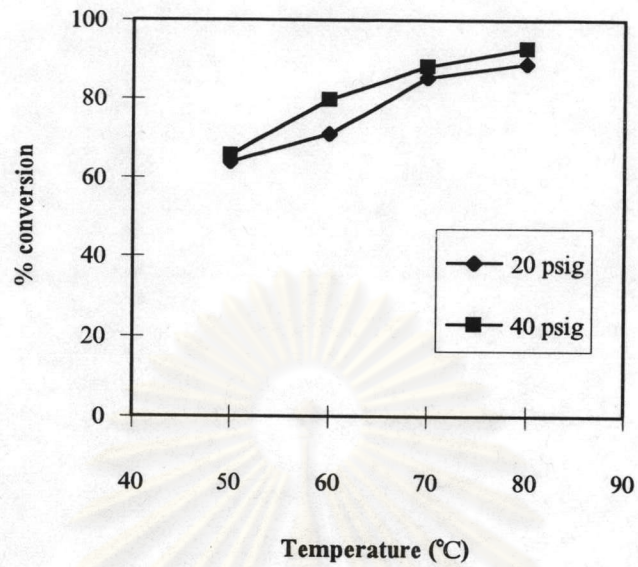


Figure 4.9 Effect of reaction temperature and pressure on the degree of monomers conversion.

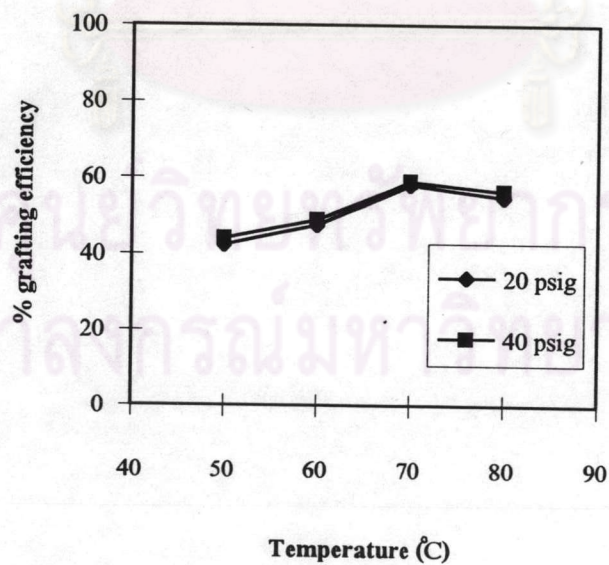


Figure 4.10 Effect of reaction temperature and pressure on the grafting efficiency.

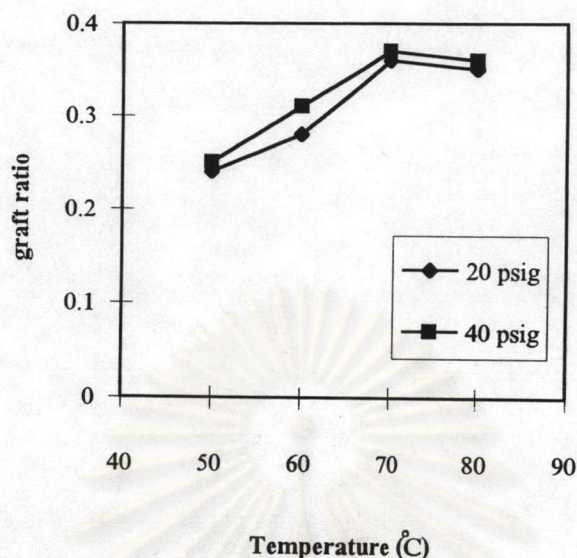


Figure 4.11 Effect of reaction temperature and pressure on the graft ratio.

4.2.3.2 Effect of Reaction Temperature and Pressure on the Free SAN Chain Length and Graft Frequency

The free SAN chain length was determined by the method of H. Nai-Jen and C.S.Donald [19]. The ungrafted SAN was clearly evidence in the low molecular weight peak, eluting at about 800-1000 sec. After appropriate peak fitting, this distribution was analyzed for molecular weight parameter using the MAXIMUM-820 software supplied with the chromatography and utilizing the results from column calibration with a narrow distribution PS standard (Scientific Polymer Products). For the reaction temperature of 50 °C and pressure of 20 psig the molecular weight of free SAN determined by GPC method were as follows : $\bar{M}_n = 90,413$, $\bar{M}_w = 107,030$, $\bar{M}_z = 126,062$, $\bar{M}_w/\bar{M}_n = 1.18$. The effect of reaction temperature and pressure on the molecular weight of free SAN is shown in Table 4.4 and Figure 4.12. The free SAN chain length is proportional with the molecular weight. The detail of all data are shown in the Appendix B.

The graft frequency is the number of backbone polymer repeating units between graft chains. The graft frequency was calculated by knowing the total number of graft chain per backbone chain, both derived from the molecular weight analysis. For the reaction temperature of 50 °C and 20 psig of pressure, 17.05 g of grafted SAN at \bar{M}_n of 90,413 (Appendix A) and 69.92 g of *cis*-1,4-polyisoprene at \bar{M}_n of 137,799 were obtained. One chain of *cis*-1,4-polyisoprene had 2026.5 repeating units. According to the calculation (Appendix A), the number of grafted chains per backbone chains was 0.37. Therefore, the graft frequency was 5,477. The details of all the above calculations are shown in the Appendix A. The effect of reaction temperature and pressure on the graft frequency is shown in Table 4.4 and Figure 4.13.

From the Figure 4.12, the molecular weight of free SAN decreased with increasing reaction temperature and pressure, but it increased at temperature above 70 °C, the MW of free SAN increased. From Table 4.6 and Figure 4.13, the graft frequency decreased with increasing reaction temperature from 50 °C to 70 °C because at high temperature and pressure, the initiator could easily form free radical and attack to the backbone. Therefore, the repeating units between grafted chain decreased with increasing the reaction temperature and pressure. At temperature above 70 °C, the stability of natural rubber latex decreased, it caused the decrease of graft frequency.

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Table 4.4 Effect of reaction temperature and pressure on molecular weight of free SAN and graft frequency

Pressure (psig)	Temp. (°C)	MW of free SAN				Graft Frequency
		\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_w/\bar{M}_n	
0	50	92,299	107,290	123,349	1.16	5,196
20	50	90,413	107,030	126,062	1.18	5,477
	60	85,303	101,969	118,887	1.19	4,405
	70	74,071	96,712	114,618	1.31	3,025
	80	84,737	102,241	109,364	1.21	3,619
40	50	80,222	95,291	109,630	1.19	4,713
	60	82,796	99,561	118,181	1.20	3,897
	70	68,432	91,572	109,364	1.13	2,739
	80	82,757	99,112	114,795	1.20	3,322

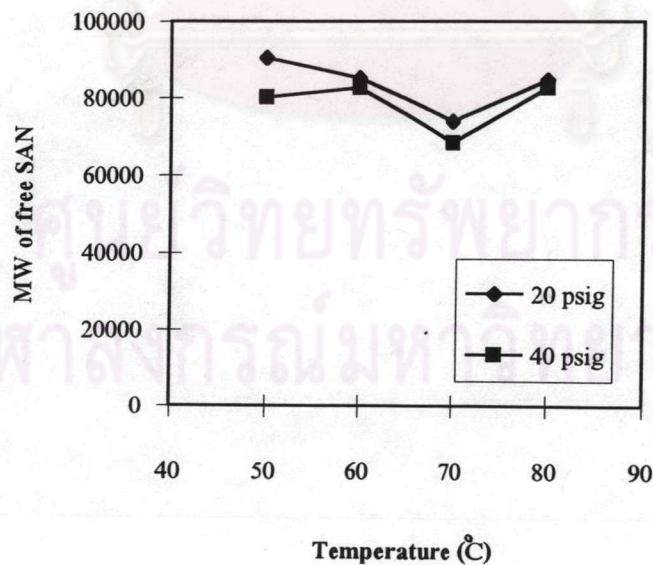


Figure 4.12 Effect of reaction temperature and pressure on molecular weight of free SAN.

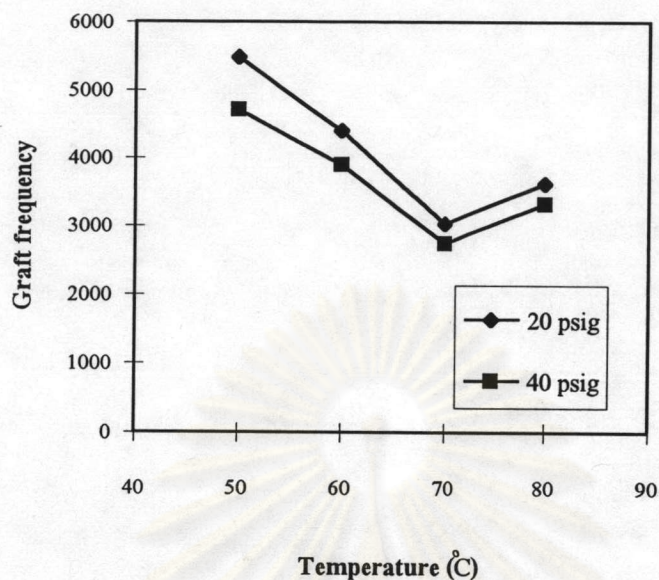


Figure 4.13 Effect of reaction temperature and pressure on the graft frequency.

4.2.3.3 Effect of Reaction Temperature and pressure on composition of grafted natural rubber

The composition of grafted natural rubber was determined by CHN/O analyzer and FT-IR. Two methods could identify the percent of styrene, acrylonitrile and isoprene in the grafted natural rubber products.

1. FT-IR measurement

FT-IR measurement was used to determine the copolymer composition by measurement of peak area, which was specified for monomer. The chemical structures of the polystyrene, polyacrylonitrile and *cis*-1,4-polyisoprene are shown in Figure 4.13.

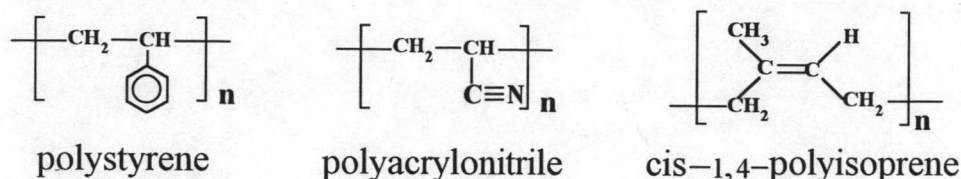


Figure 4.14 Chemical structures of polystyrene, polyacrylonitrile and *cis*-1,4-polyisoprene.

The styrene/acrylonitrile/isoprene ratio of grafted natural rubber was determined by peak area of FTIR spectra.

peak area at

810 cm^{-1}	: $\text{R}_2\text{C}=\text{CHR}$ of <u>isoprene</u>
1510 cm^{-1}	: $\text{C}=\text{C}$ stretching of benzene ring of <u>styrene</u>
2238 cm^{-1}	: $\text{C}\equiv\text{N}$ stretching of <u>acrylonitrile</u>

The determination of the ratio of acrylonitrile, isoprene and styrene in the grafted natural rubber by FT-IR measurement was not accurate because the peak area of $\text{C}=\text{C}$ stretching of benzene ring at 1500 cm^{-1} , was shielded by the peak area of $\text{C}-\text{H}$ bending of CH_3 in the structure of *cis*-1,4-polyisoprene. Therefore, the determination of the ratio of acrylonitrile, isoprene and styrene in grafted natural rubber must be determined by two steps. First step was to find the ratio of acrylonitrile and styrene from the free SAN which was extracted from the graft products. In this step, the ratio of acrylonitrile and styrene in the free SAN which separated from graft products was assumed to be equal to the ratio of acrylonitrile and styrene in the grafted natural rubber. The result of A/S ratio from the first step was used to determine the ratio of acrylonitrile, isoprene and styrene of grafted natural rubber in the second step.

I) First Step

The ratio of acrylonitrile and styrene in the free SAN was determined. The sample was prepared by casting on the KBr cell. The FT-IR spectrum of free SAN is shown in Appendix C. The ratios of acrylonitrile and styrene in free SAN are shown in Table CI at various reaction temperature and pressure.

II) Second Step

The ratios of acrylonitrile, isoprene and styrene in grafted natural rubber were determined. The preparation of the samples was the same as in the first step. Results from the FTIR measurement reported the peak area of isoprene ($R_2C=CHR$ at 810 cm^{-1}) and acrylonitrile ($C\equiv N$ at 2238 cm^{-1}) as shown in Table CI. From the FTIR spectrum of free SAN at the reaction temperature of $50\text{ }^\circ\text{C}$ and pressure of 20 psig, peak areas of acrylonitrile and styrene were 301.054 and 237.063, respectively. From the FTIR spectrum of graft natural rubber produced at the reaction temperature of $50\text{ }^\circ\text{C}$ and 20 psig of pressure, peak areas of isoprene and acrylonitrile were 671.315 and 171.309, respectively. Therefore, the peak area of styrene in the graft natural rubber was calculated by $(171.309)(237.063/301.054) = 134.896$. The ratios of acrylonitrile, isoprene and styrene in the grafted natural rubber are shown in Table 4.5. The details of all data are shown in Appendix C.

2. CHN\O Analyzer

CHN\O analyzer was also used to measure and calculate the copolymer composition. The ratios of styrene and acrylonitrile in the grafted natural rubber were calculated as shown in Figures 4.15 and 4.16. The ratios of acrylonitrile, isoprene and styrene monomers were calculated by using number of mole according to C, H, N and O in the grafted natural rubber obtained from the analysis. Effect of reaction temperature and pressure on composition of grafted natural rubber is shown in Table 4.5. The details of all data and calculations are shown in Appendix D.

From Figures 4.15 and 4.16 show the effect of reaction temperature and pressure on the ratio of styrene and acrylonitrile in the grafted natural rubber. The acrylonitrile content increased with increasing the reaction temperature from $50\text{ to }70\text{ }^\circ\text{C}$ and reached the maximum value at $70\text{ }^\circ\text{C}$. At the reaction temperature above $70\text{ }^\circ\text{C}$, the acrylonitrile content decreased. The styrene content increased with increasing the reaction temperature.

The interesting finding in this work is the technique for the determination of copolymer composition of grafted natural rubber. Table 4.5, Figure 4.15 and 4.16

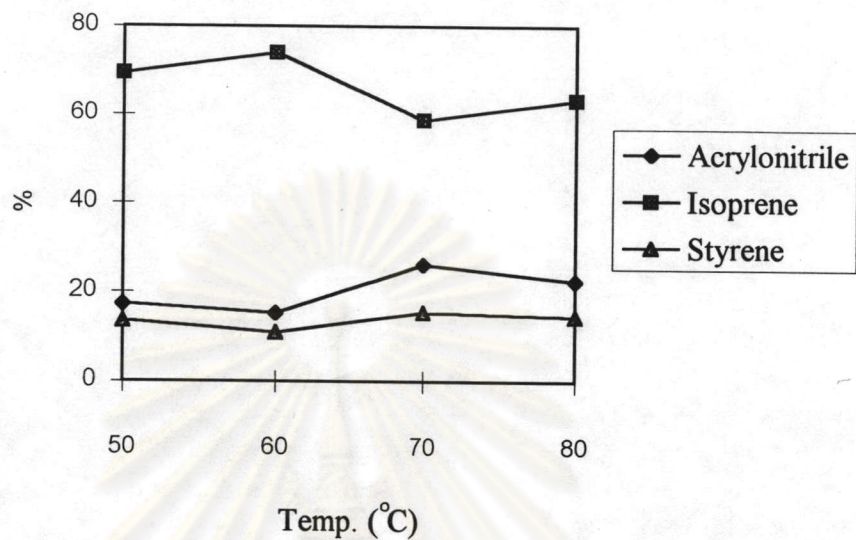
show that the results of these two techniques are acceptable. The results confirm that the FT-IR method and CHN/O method are suitable for this measurement.

Table 4.5 Effect of reaction temperature and pressure on the composition of grafted natural rubber.

Pressure (psig)	Temp (°C)	Acrylonitrile/Isoprene/Styrene	
		FT-IR method	CHN/O method
0	50	16.0 : 75.5 : 8.5	18.9 : 69.2 : 11.9
20	50	17.2 : 69.3 : 13.5	19.1 : 68.1 : 12.8
	60	15.2 : 73.9 : 10.9	16.5 : 72.7 : 10.8
	70	26.0 : 58.7 : 15.3	26.6 : 62.2 : 11.2
	80	22.4 : 63.2 : 14.4	21.4 : 63.6 : 15.0
40	50	18.5 : 65.4 : 16.1	19.6 : 68.5 : 11.9
	60	15.5 : 75.5 : 9.0	18.0 : 69.8 : 12.2
	70	29.8 : 55.0 : 15.2	26.4 : 61.8 : 11.8
	80	27.7 : 58.2 : 14.1	26.3 : 62.4 : 11.3

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a) FT-IR Measurement



b) CHN\O Analyzer

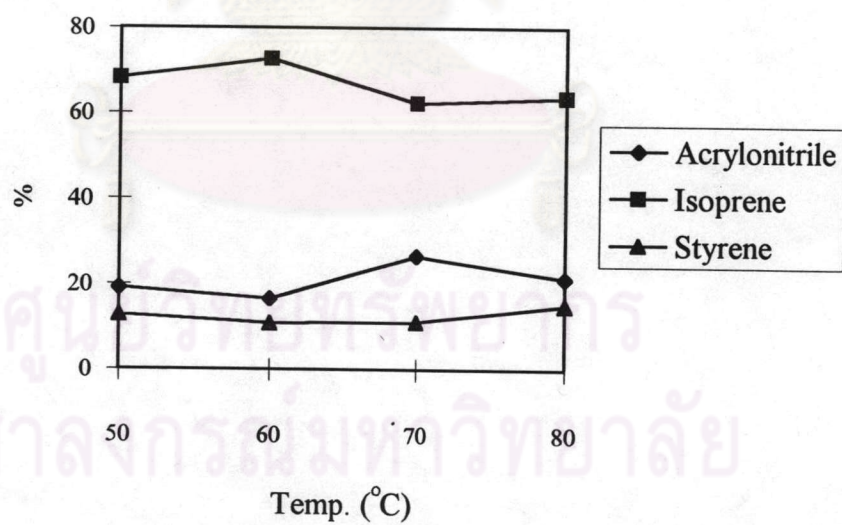
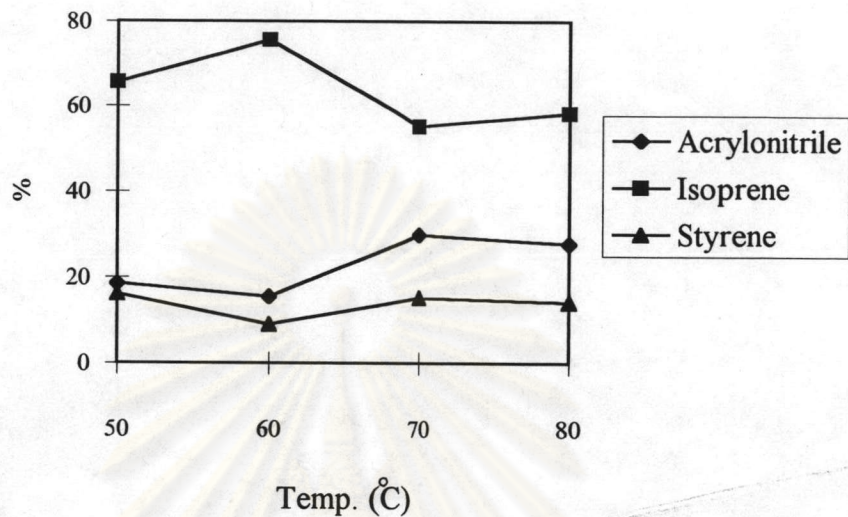


Figure 4.15. Effect of reaction temperature on the composition of grafted natural rubber at pressure of 20 psig.

a) FTIR measurement. b) CHN\O analyzer

a) FT-IR Measurement



b) CHN\O Analyzer

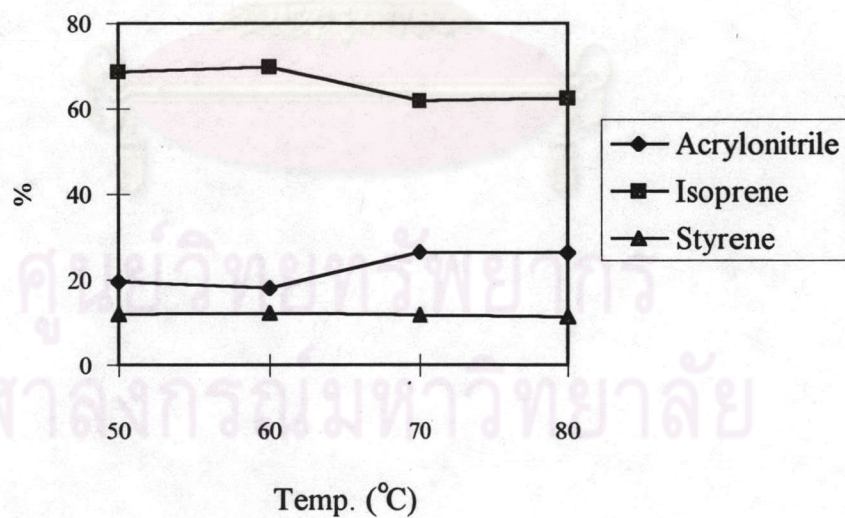


Figure 4.16. Effect of reaction temperature on the composition of grafted natural rubber at pressure of 40 psig.

a) FTIR measurement. b) CHN\O analyzer.

The purpose of this study is to obtain the appropriate condition which yield the grafted natural rubber with had desirable properties. From Table 4.3, 4.4, and 4.5, the reaction temperature of 70 °C and the pressure range of 20 to 40 psig gave the grafted natural rubber which had high grafting efficiency, graft ratio, acrylonitrile and styrene ratio and frequency of graft chain on 70 °C and 30 psig. And the monomer conversion was high at this condition. The characteristic and composition of the grafted natural rubber which prepared at 70 °C 30 psig is shown in Table 4.6.

Table 4.6 The characteristic of the grafted natural rubber (70 °C and 30 psig)

Grafting Properties	Grafted Natural Rubber (70 °C, 30 psig)
Monomers conversion	88.9
Grafting efficiency	45.4
Graft Ratio	0.45
Graft frequency	2,413
MW of free SAN	61,522
<u>Composition</u>	
A : I : S (FT-IR method)	28.9 : 55.2 : 15.9
A : I : S (CHN\O)	27.2 : 59.4 : 12.9

From Table 4.6, the appropriate condition for preparation of grafted natural rubber was 70 °C and 30 psig which gave high monomers conversion, grafting efficiency and acrylonitrile content in graft copolymer.

4.3 Thermal Properties of Grafted Natural Rubber

In this study, Differential Scanning Calorimetry (DSC), was used to obtain the T_g of the grafted natural rubber. Figure 4.17 shows DSC thermogram of the grafted natural rubber polymerized at 70 °C and pressure of 30 psig. The DSC measurements showed that T_g of natural rubber was at -57.4 °C and single narrow transitions exhibited at 97.1 °C, which indicated the random copolymers of styrene and acrylonitrile.[26]

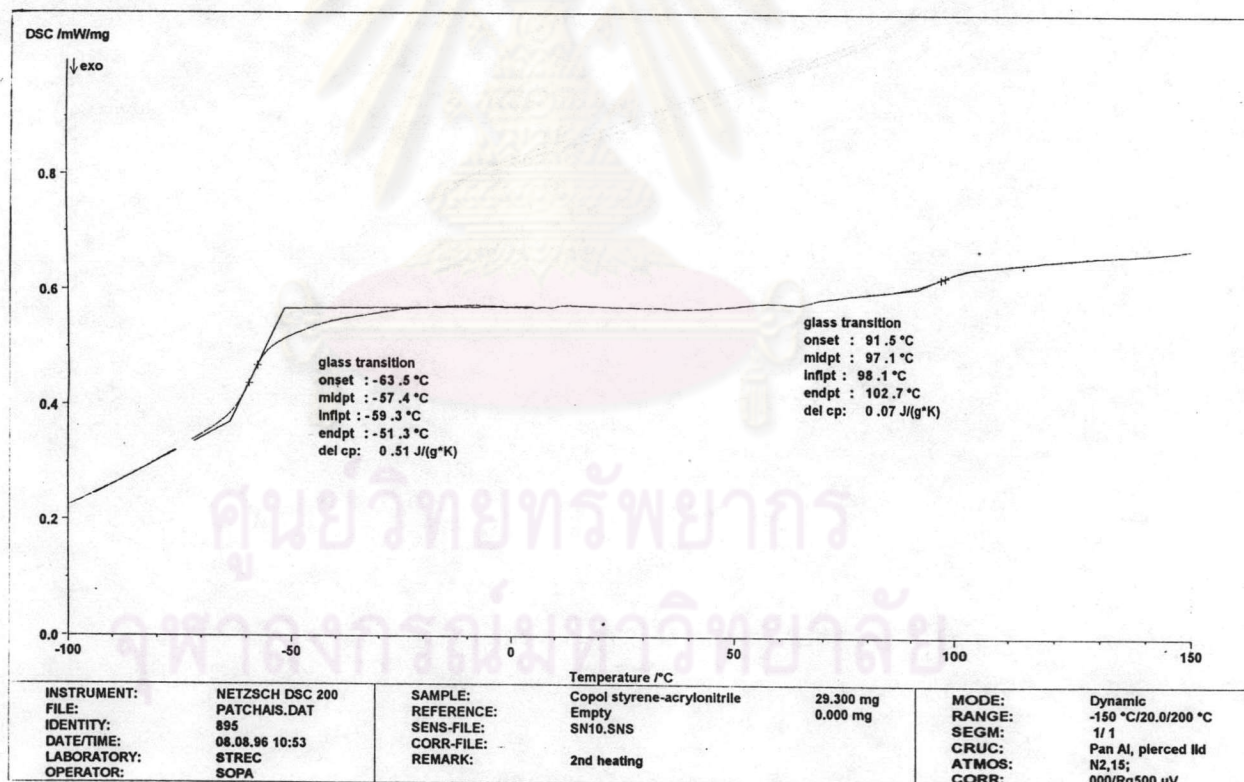


Figure 4.17 DSC thermogram of the grafted natural rubber : polymerization at 70 °C, 30 psig. for 8 hours.

4.4 Mechanical Properties of Thermoplastic Blends

For the preparation of a thermoplastic blends, the grafted natural rubber was blended with SAN. The graft copolymerization of styrene and acrylonitrile on natural rubber latex was carried on at 70 °C 30 psig for 8 hours. After the addition of 1.0 part of a phenolic antioxidant, the graft latex was coagulated, then casted and washed. Finally, the grafted rubber sheet was dried at 40 °C in vacuum oven. The grafted natural rubber was blended with SAN ($\bar{M}_n = 68,340$, $\bar{M}_w = 127,100$, $\bar{M}_w/\bar{M}_n = 1.86$) at various ratios and 0.1 part of silicone oil, in the 2-rolls mill. The blend was then injection molded to give the standard bar and the sheet.

Table 4.7 and Figure 4.17 illustrate the effect of the grafted natural rubber content on the mechanical properties. The mechanical properties decreased with increasing the grafted natural rubber content. This effect may be attributed to the process of blending of graft natural rubber with SAN. The process of blending consisted of three steps. The first step was to blend the grafted natural rubber with SAN in the 2-rolls mill at 180 °C for 15 min. The second step was to cut the sheet into small chips by cutting machine. The third step was to obtain the standard bar and the sheet by injection molding at nozzle temperature of 220 °C. Therefore, some portion of rubber was possibly degraded, because the color of the sample was observed at each step. The more grafted natural rubber content, the lower the mechanical properties of the blends.

ABS MH-3 (commercial grades) have suitable properties for using in the plastic industry. Their properties were obtained by adding suitable additives. The properties of blended thermoplastic were slightly lower than those because the preparation of these thermoplastic blends were performed without additive adding.

Table 4.7. Effect of grafted natural rubber content on the mechanical properties of the thermoplastic blends.

Property	ASTM Test method	Blending of graft NR : SAN				SAN (120PC)	ABS (MH-3)
		20:80	30:70	40:60	50:50		
Tensile strength, MPa	D634	31.0 ± 0.7	30.9 ± 0.4	23.6 ± 0.3	20.9 ± 0.5	51.4 ± 1.1	32.5 ± 0.4
Elongation at break (%)	D634	2.5 ± 0.2	12.1 ± 1.3	10.3 ± 0.5	8.4 ± 0.2	1.7 ± 0.2	2.4 ± 0.1
Izod notched impact strength J/m	D256	16.6 ± 0.2	12.8 ± 0.9	12.7 ± 0.2	16.7 ± 0.7	6.5 ± 0.5	52.0 ± 2.6
Rockwell hardness, R-scale	D785	75.4 ± 0.9	73.7 ± 0.8	70.9 ± 0.6	69.4 ± 0.5	84.4 ± 0.4	77.2 ± 0.3

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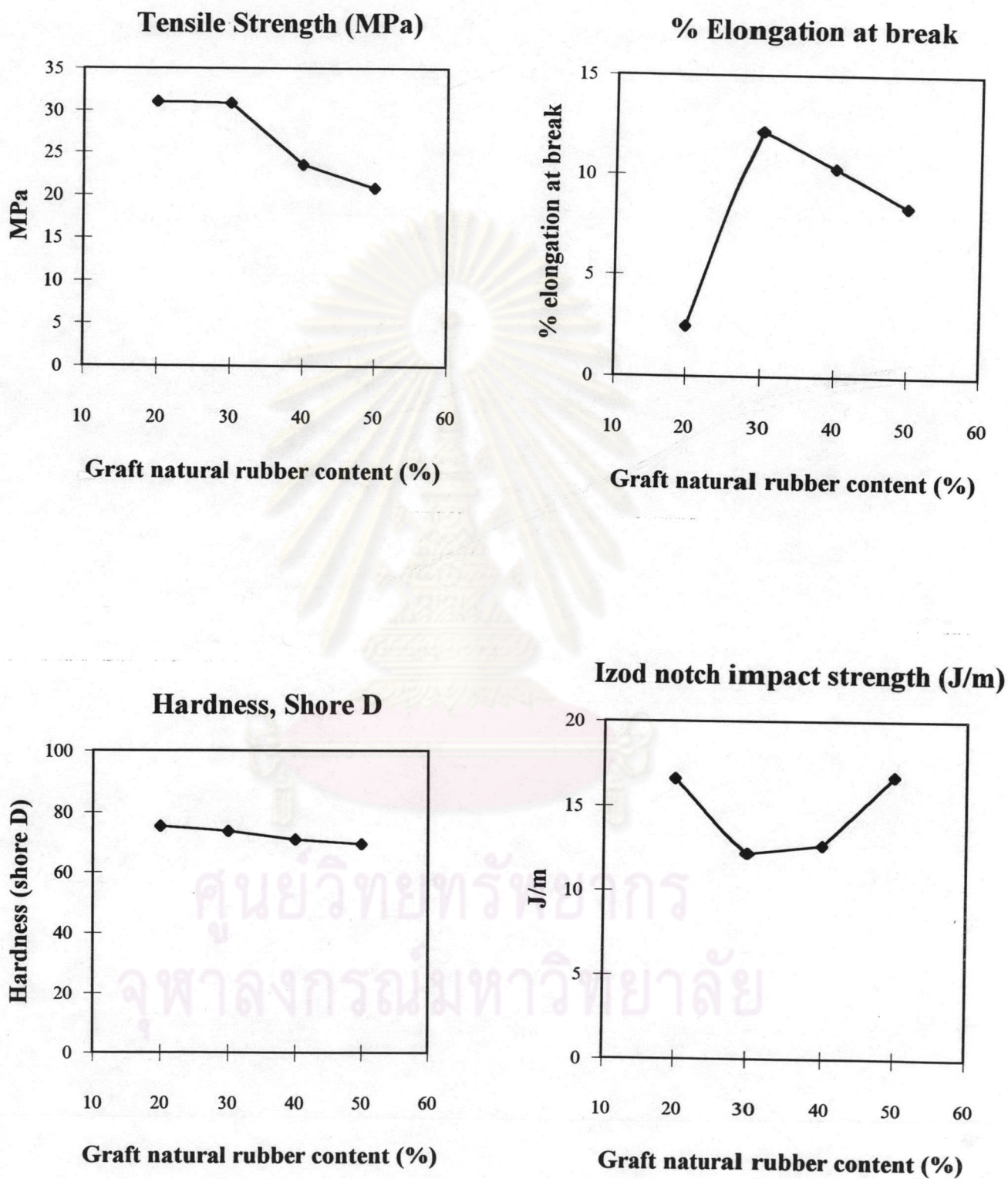


Figure 4.18 Effect of grafted natural rubber content on mechanical properties of