

## CHAPTER IV

### RESULTS AND DISCUSSION

In the present work, graft copolymer of styrene and acrylonitrile on natural rubber was synthesized by using the emulsion polymerization. The blends of graft natural rubber and SAN were prepared and the physical properties of the blends were investigated.

#### Properties of Raw Natural Rubber Latex

##### 1. Properties of 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 60.5 %. The typical properties of natural rubber latex is shown in Table 4.1. The molecular weight of natural rubber determined by the GPC are as follows :  $\bar{M}_n = 135,702$ ,  $\bar{M}_w = 762,858$ ,  $\bar{M}_z = 1,772,839$   $\bar{M}_w/\bar{M}_n = 5.62$ .

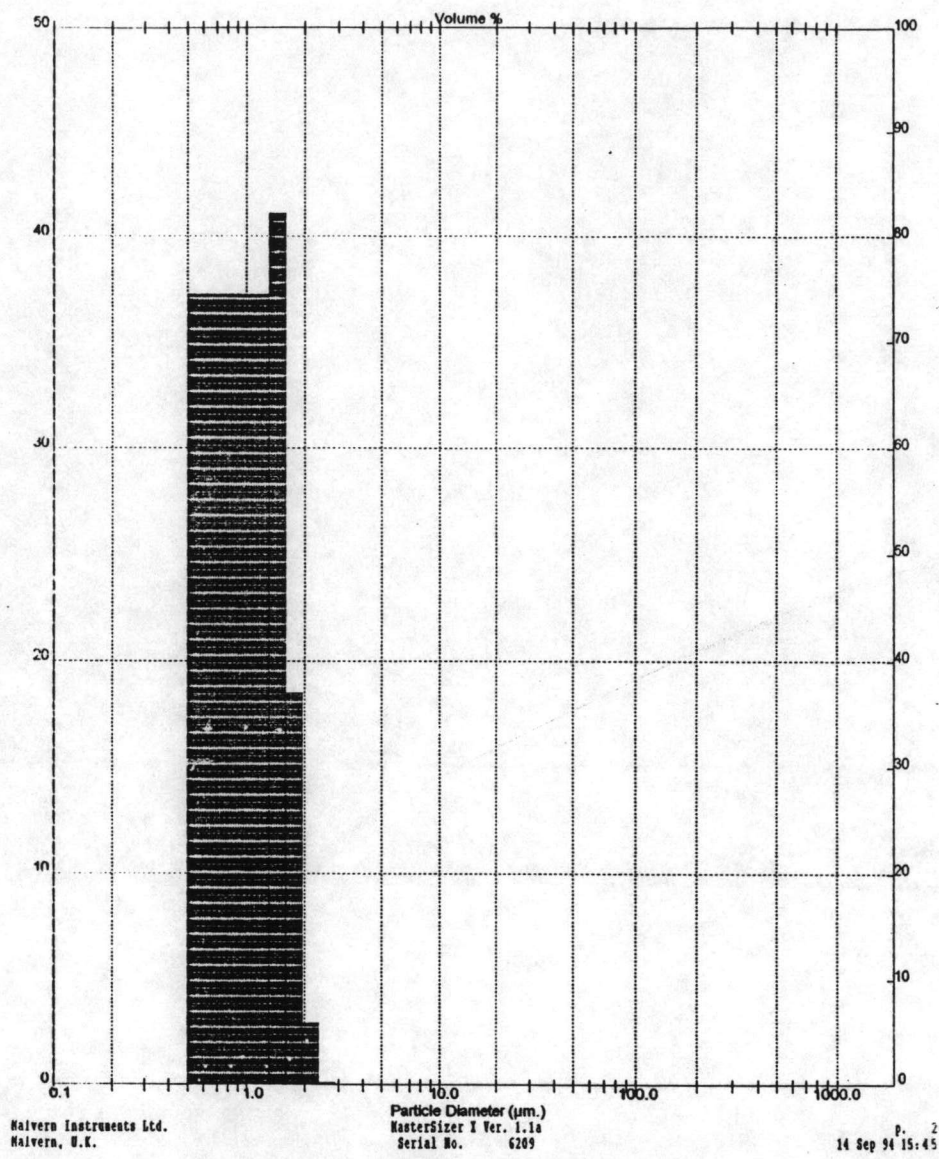
**Table 4.1.** The properties of natural rubber latex : high ammonia.

Properties	Tested results
Total Solid Content ,%	62.45
Dry Rubber Content ,%	60.04
Non Rubber Solid ,%	1.41
Ammonia Content (on Total Weight) ,%	0.72
Ammonia Content (on Water phase) ,%	1.87
pH Value	10.48
KOH Number	0.51
Volatile Fatty Acid Number (VFA)	0.0205
Mechanical Stability Time @ 55% TS., (sec)	1,040
Specific Gravity at 25 C°	0.9450
Magnesium Content (solid form)	37 ppm

Source : Thai Rubber Latex Corporation (Thailand) Public co., Ltd. Bangplee Samutprakarn. Tel 316-4277-80

## 2. Determination of Particle Sizes

The average diameter and size distribution of rubber particle were determined by the mastersizer as shown in figure 4.1.



Size (Lo) µm	Result In %	Size (Hi) µm	Result Below %
0.50	37.36	1.32	37.36
1.32	40.74	1.60	78.10
1.60	18.74	1.95	96.84
1.95	3.03	2.38	99.87
2.38	0.13	2.90	100.00
2.90	0.00	3.53	100.00
3.53	0.00	4.30	100.00
4.30	0.00	5.24	100.00
5.24	0.00	6.39	100.00
6.39	0.00	7.78	100.00
7.78	0.00	9.48	100.00
9.48	0.00	11.55	100.00
11.55	0.00	14.08	100.00
14.08	0.00	17.15	100.00
17.15	0.00	20.90	100.00
20.90	0.00	25.46	100.00

Size (Lo) µm	Result In %	Size (Hi) µm	Result Below %
25.46	0.00	31.01	100.00
31.01	0.00	37.79	100.00
37.79	0.00	46.03	100.00
46.03	0.00	56.09	100.00
56.09	0.00	68.33	100.00
68.33	0.00	83.26	100.00
83.26	0.00	101.44	100.00
101.44	0.00	123.59	100.00
123.59	0.00	150.57	100.00
150.57	0.00	183.44	100.00
183.44	0.00	223.51	100.00
223.51	0.00	272.31	100.00
272.31	0.00	331.77	100.00
331.77	0.00	404.21	100.00
404.21	0.00	492.47	100.00
492.47	0.00	600.00	100.00

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

Saunter mean : 1.16 µm

Specific surface area : 5.1633 sq.m./gm

Diameter : 1.07 µm

## Preparation of Graft Natural Rubber

The natural rubber latex, which have average particle size about  $1.07 \mu\text{m}$  was employed in the grafting by emulsion polymerization process. In this work,  $\text{K}_2\text{S}_2\text{O}_8$  (potassium persulfate) was used as initiator. Graft copolymerization initiated by the reaction between  $\text{K}_2\text{S}_2\text{O}_8$  and styrene yielded styrene radical which could abstract a hydrogen atom from rubber backbone resulting in a rubber macroradical. The rubber macroradical then with styrene and acrylonitrile monomers to form graft copolymer [18]. The particle structure of grafted rubber latex was of the core-shell type [3, 28].

In the preparation of graft copolymer of acrylonitrile and styrene onto natural rubber latex, appropriate conditions which yielded high percent conversion and high grafting efficiency were investigated. The topics investigated in this research work are as follows :

- 1) Effect of monomer content
- 2) Effect of emulsifier concentration
- 3) Effect of reaction temperature



### 1) Effect of Monomer Content

The preparation of graft natural rubber was performed by emulsion polymerization process. In this case, the natural rubber latex was as an seed latex of *cis*-1,4-polyisoprene which as the isoprene monomer was polymerized first, and acrylonitrile and styrene monomers 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 elastomer 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 [28]. Emulsion grafted to 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. If the closed shell of grafted rubber latex was formed incompletely, coagulation in the acid solution would be occur pursuant.

The graft copolymerization was carried out by adding various amount of styrene and acrylonitrile monomers on the rubber content. For 1.5 part by weight of emulsifier, per 100 parts of natural rubber, the reaction condition was at 65 °C for 8 hours. The complete formation of core-shell was tested by the coagulation reaction of graft latex in acid solution. If the formation was complete, the coagulation would not occur. The results of the graft copolymerization are summarized in Table 4.2.

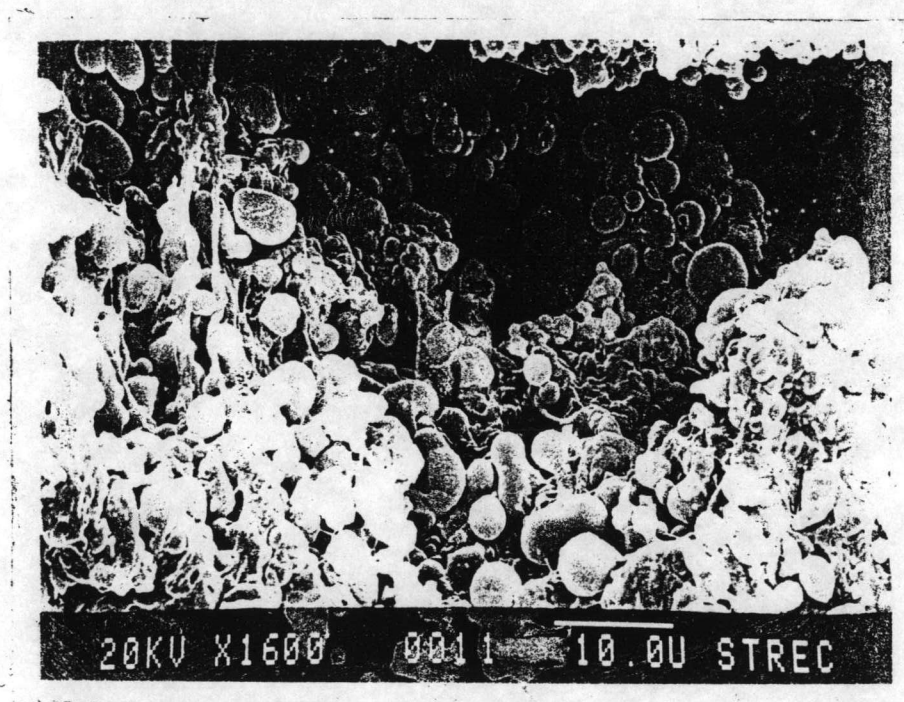
The result indicated that the complete closed shell formed at above 100 parts by weight of monomers. At the reaction time of 8 hours and 100 parts by weight of monomers, some coagulations of large particles occurred partially as shown in Figure 4.2. The results of core-shell formation and the dispersion of particles of graft latex are shown in Figures 4.3 and 4.4, respectively.

**Table 4.2.** Effect of styrene and acrylonitrile monomers content on the closed shell of graft natural rubber latex.

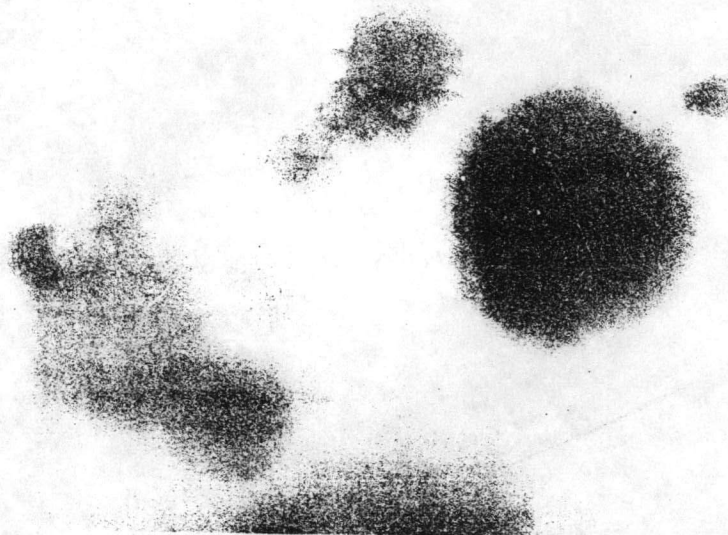
Expt. No	Parts by weight			Coagulation in acid solution
	Natural Rubber	Acrylonitrile	Styrene	
1	100	12	18	+
2	100	20	30	+
3	100	30	45	+,-
4	100	40	60	-
5	100	60	90	-
6	100	80	120	-

+ : The graft natural rubber latex were coagulated in the acid solution

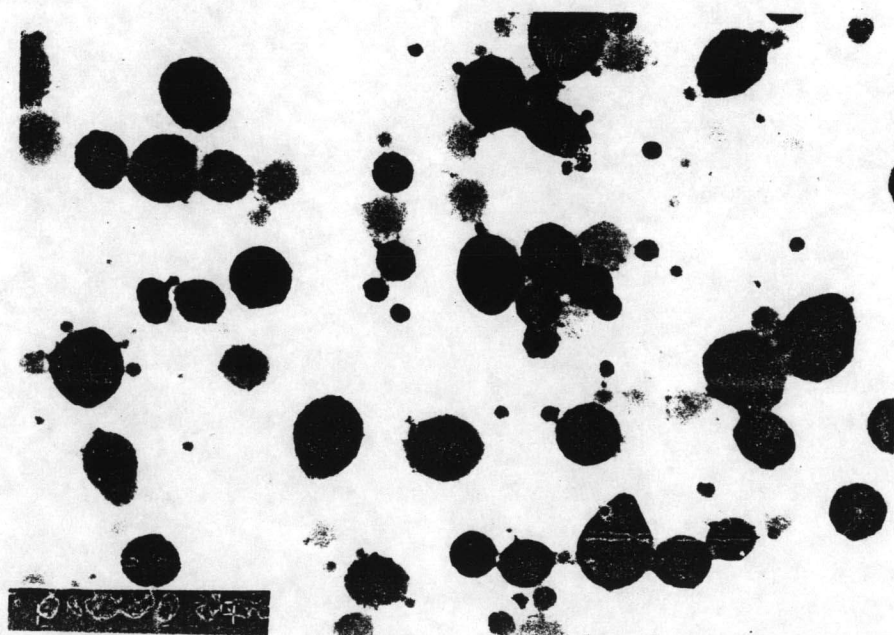
- : The graft natural rubber latex were not coagulated in the acid solution



**Figure 4.2.** Scanning Electron Micrograph of seed particles from emulsion polymerization of graft natural rubber latex before stop reaction.



**Figure 4.3.** Transmission Electron Micrograph of completed closed shell of graft natural rubber latex.



**Figure 4.4.** Transmission Electron Micrograph of graft natural rubber latex.

## 2) Effect of Emulsifier Concentration

Effect of emulsifier concentration on degree of monomer conversion, grafting efficiency, and graft ratio were investigated by varying the emulsifier concentration of 1.0, 1.5, 2.0 parts by weight ( per 100 parts of rubber content). The appropriate amounts of the styrene and acrylonitrile monomers (60 :40) together were at 100 parts by weight per 100 parts of rubber content. The reaction condition was at 65 °C, 8 hours.

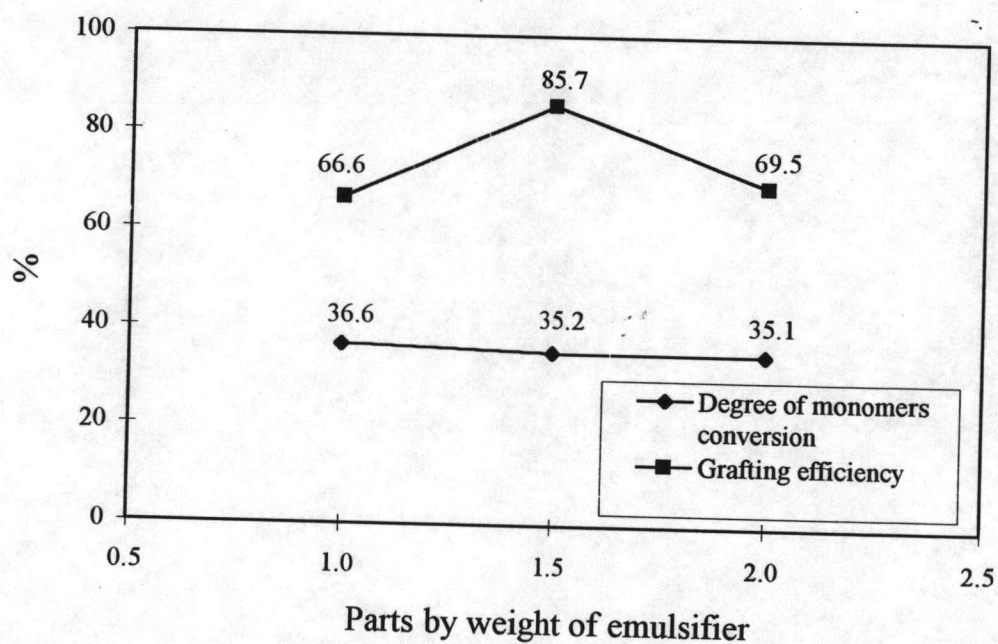
The degree of monomers conversion is defined as the mass of SAN formed (grafted and free) divided by the initial mass of monomers. The grafting efficiency is readily defined as the mass of the grafted SAN divided by the total mass of grafted latex produced. The graft ratio is calculated from the mass of styrene and acrylonitrile monomers which grafted on the backbone polymer divided by the rubber which formed graft with styrene and acrylonitrile monomers [18]. The detail of all of the above data and calculations are shown in the Appendix B. The effect of emulsifier concentration on the graft properties is summarized in Table 4.3 and Figure 4.5.

The maximum value of grafting efficiency was 85.7 % at 1.5 parts by weight of emulsifier. The variation of emulsifier concentration did not affect the degree of monomers conversion. At high emulsifier concentration (2 part) the free micelle without rubber could be formed and ungraft copolymer was also formed therefore, the grafting efficiency and graft ratio decreased. At low emulsifier concentration (1 part), the formation of micelle on the surface area of rubber latex was incomplete because some portion of rubber was coagulated before the addition of monomers [28], therefore the grafting efficiency and the graft ratio decreased.



**Table 4.3.** Effect of emulsifier concentration on grafting properties.

Grafting properties	Parts by weight of emulsifier		
	1.0	1.5	2.0
Degree of monomers conversion (%)	36.6	35.2	35.1
Grafting efficiency (%)	66.6	85.7	69.5
Graft ratio (g.g <sup>-1</sup> )	0.11	0.38	0.21

**Figure 4.5.** Effect of emulsifier concentration on the degree of monomers conversion and grafting efficiency.

### 3) Effect of Reaction Temperature

The reaction temperature had a strong effect on the graft natural rubber product, because the reaction temperature affected the reactivity ratio of monomers and the ratio of acrylonitrile and styrene monomers in aqueous phase. In this study, the effect of reaction temperature on the synthesis of graft natural rubber was investigated by varying the reaction temperature at 30, 40, 50, and 65 °C. The effect of reaction temperature on the graft characteristics, the copolymer composition and the thermal properties of graft natural rubber were investigated.

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

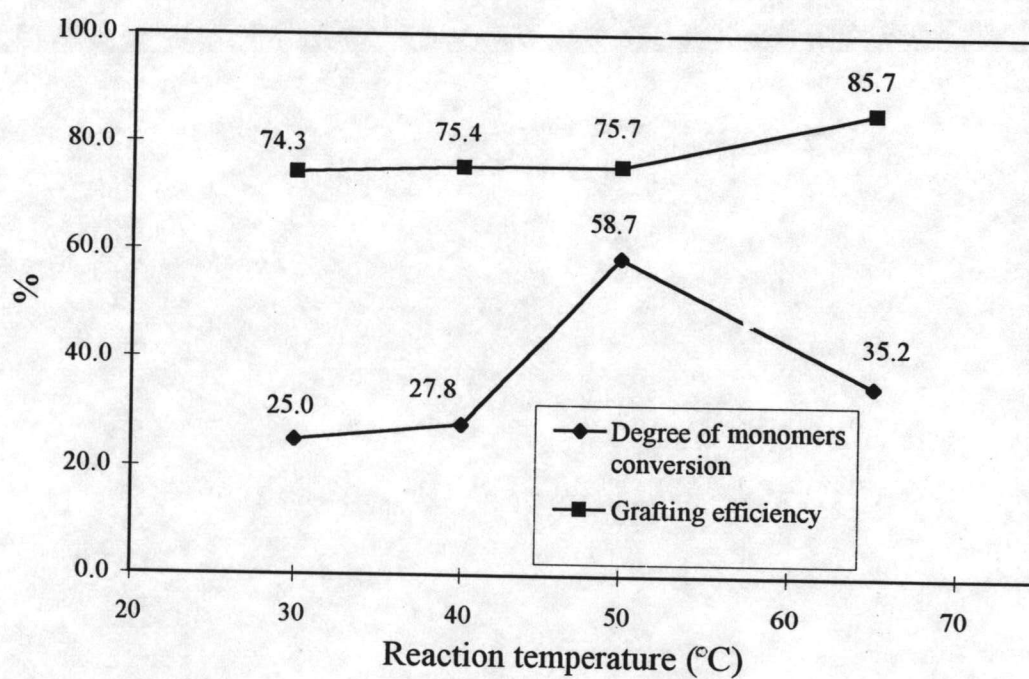
Rubber content	: 100 parts by weight.
AS monomers content	: 100 parts by weight.
Ratio of acrylonitrile and styrene	: 40 : 60
Emulsifier	: 1.5 parts by weight.

#### 3.1 Effect of reaction temperature on the graft characteristics

The graft characteristics of graft natural rubber reported are degree of monomers conversion, grafting efficiency, graft ratio, free SAN chain length, and graft frequency. The graft characteristics of graft natural rubber at various reaction temperatures were shown in Table 4.4 and Figure 4.6. The detail of all data and calculations are shown in appendix CI.

**Table 4.4.** Effect of reaction temperature on grafted characteristics of graft natural rubber.

Graft characteristics	Reaction temperature (°C)			
	30	40	50	65
Degree of monomers conversion (%)	25.0	27.8	58.7	35.2
Grafting efficiency (%)	74.3	75.4	75.7	85.7
Graft ratio (g.g <sup>-1</sup> )	0.29	0.29	0.64	0.38



**Figure 4.6.** Effect of reaction temperature on the degree of monomers conversion and grafting efficiency.

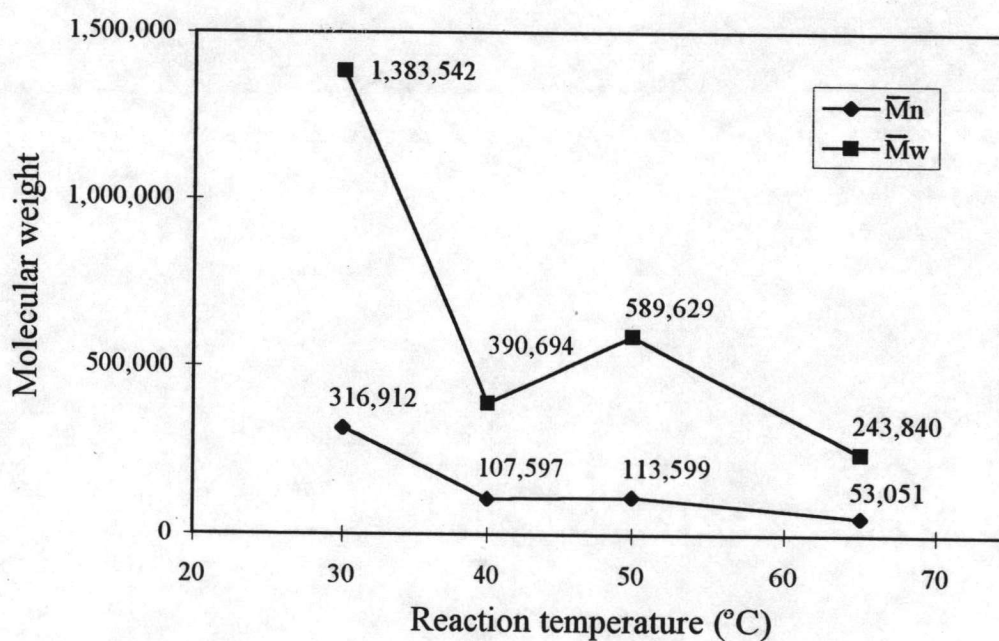
From Figure 4.6 the grafting efficiency and graft ratio increased slightly with increasing reaction temperature. The degree of monomers conversion increased with increasing reaction temperature from 30 to 50 °C. The maximum degree of monomers conversion was 58.6 % at 50 °C. At the reaction temperature above 50 °C, the degree of monomers conversion would decrease, whereas the grafting efficiency and graft ratio increased.

### 3.2 Effect of reaction temperature on the free SAN chain length

The free SAN chain length was determined by the method of H. Nai-Jen and C.S. Donald [18]. The ungrafted SAN was clearly evidence in the low molecular weight peak, eluting at about 1,200-2,000 sec. After appropriate peak fitting, this distribution was analyzed for molecular weight parameter using the MAXIMUM-820 software supplied with the chromatograph and utilizing the results from column calibration with a narrow distribution PS standard (Scientific Polymer Products). For the reaction temperature of 40 °C the molecular weight of free SAN determined by GPC method were as follows :  $\bar{M}_n = 107,597$ ,  $\bar{M}_w = 390,694$ ,  $\bar{M}_z = 893,813$  and  $\bar{M}_w/\bar{M}_n = 3.63$ . The effect of reaction temperature on the molecular weight of free SAN is shown in Table 4.5 and Figure 4.7. The detail of all data and calculations are shown in the Appendix CII.

**Table 4.5.** Effect of reaction temperature on the molecular weight of free SAN.

Molecular weight	Free SAN at reaction temperature (°C)			
	30	40	50	65
$\bar{M}_n$	316,912	107,597	113,599	53,051
$\bar{M}_w$	1,383,542	390,694	589,629	243,840
$\bar{M}_z$	3,035,832	893,813	1,702,689	647,890
$\bar{M}_w/\bar{M}_n$	4.36	3.63	5.19	4.59



**Figure 4.7.** Effect of reaction temperatures on  $\bar{M}_w$  and  $\bar{M}_n$  of free SAN separated from grafted products.

### 3.3 Effect of reaction temperature on the graft frequency

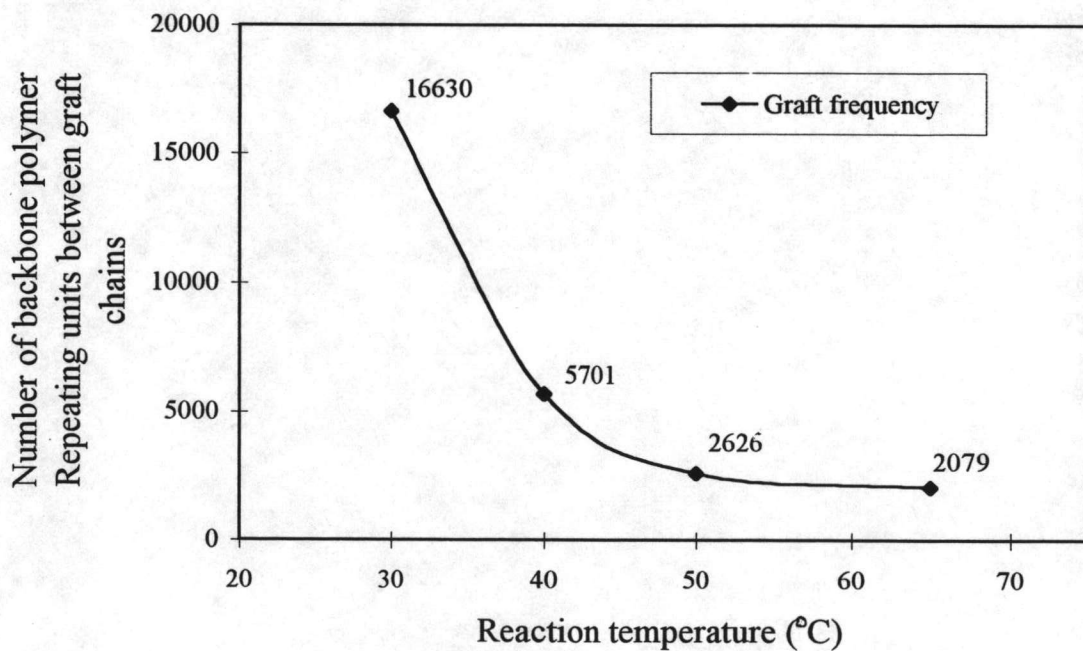
The graft frequency is the number of backbone polymer repeating units between graft chains. The graft frequency was calculated by knowing the total number of graft chain per backbone chain, both derived from the molecular weight analysis. For the reaction temperature of 30 °C, 37.5 g of free SAN at  $\bar{M}_n$  of 316,912 (Table 4.5) and 130 g of *cis*-1,4-polyisoprene at  $\bar{M}_n$  of 135,702 (Table 4.5) were obtained. One molecular chain of *cis*-1,4-polyisoprene had 1995.6 (135,702/68) repeating units. According to the calculation (Appendix CIII), the number of grafted chains per backbone chains was 0.12. Therefore, the graft frequency was 16,630. The details of all the above calculations are shown in the Appendix CIII. The effect of reaction temperature on the graft frequency is shown in Table 4.6 and Figure 4.8.

The value of graft frequency decreased with increasing reaction temperature because at high temperature, the initiator could easily form free radical. Therefore, the repeating units between grafted chains decreased with increasing the reaction temperature.



**Table 4.6.** Effect of reaction temperatures on the graft frequency.

Graft parameter	Reaction temperature ( °C)			
	30	40	50	65
Degree of monomers conversion (%)	25.0	27.8	58.7	35.2
Grafting efficiency (%)	74.3	75.4	75.7	85.7
Weight of SAN graft chains (g)	37.5	39.0	79.9	56.6
Weight of rubber backbone (g)	130.0	134.3	125.4	150.7
Number of SAN graft chains x Avogardo number x 10 <sup>-4</sup>	1.18	3.62	7.03	10.7
Number of rubber backbone x Avogardo number x 10 <sup>-4</sup>	9.58	10.3	9.24	11.1
Graft frequency	16,630	5,701	2,626	2,079



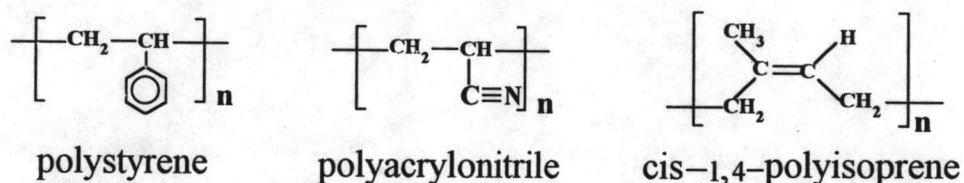
**Figure 4.8.** Effect of reaction temperature on the number of backbone polymer repeating units between graft chains (graft frequency).

## Copolymer Composition of Graft Natural Rubber

Effect of reaction temperature on the copolymer composition of graft natural rubber was determined by measurement of the peak area, which was specified for repeating unit of each monomer in FTIR spectroscopy [Appendix D]. The copolymer composition was also calculated by CHNO method. Graft copolymers used in the determination produced by emulsion polymerization using acrylonitrile and styrene ratio of 40 : 60 and AS monomers content 100 parts per 100 parts of rubber.

### 1. FTIR measurement

FTIR measurement was used to determine the copolymer composition. The chemical structures of the polystyrene, polyacrylonitrile and *cis*-1,4-polyisoprene are shown in Figure 4.9.



**Figure 4.9.** Chemical structures of polystyrene, polyacrylonitrile and *cis*-1,4-polyisoprene.

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

#### peak area at

- 810 cm<sup>-1</sup> : R<sub>2</sub>C=CHR of isoprene
- 1510 cm<sup>-1</sup> : C=C stretching of benzene ring of styrene
- 2238 cm<sup>-1</sup> : C≡N stretching of acrylonitrile



The determination of the ratio of acrylonitrile, isoprene and styrene in the graft natural rubber by FTIR measurement was not accurate because the peak area of  $C=C$  stretching of benzene ring at  $1500\text{ cm}^{-1}$ , was shielded by the peak area of C-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 graft natural rubber must be determined by two steps. First step was to find the ratio of acrylonitrile and styrene from the free SAN which 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 graft natural rubber. The result of A/S ratio from the first step was used to determine the ratio of acrylonitrile, isoprene and styrene of graft 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 NaCl cell. The ratio of peak area for acrylonitrile and styrene is shown in appendix D. The ratios of acrylonitrile and styrene in free SAN are shown in Table 4.7 at various reaction temperatures.

#### II) Second Step

The ratios of acrylonitrile, isoprene and styrene in graft 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  $810\text{ cm}^{-1}$ ) and acrylonitrile ( $C\equiv N$  at  $2238\text{ cm}^{-1}$ ) as shown in Table AII. From the FTIR spectrum of free SAN, peak areas of acrylonitrile and styrene were 3.133 and 3.165, respectively. From the FTIR spectrum of graft natural rubber produced at the reaction temperature of  $30\text{ }^\circ\text{C}$ , peak areas of isoprene and acrylonitrile were 13.412 and 1.504, respectively. Therefore, the

peak area of styrene in the graft natural rubber was calculated by  $(1.504) (3.165/3.133) = 1.065$ . The ratios of acrylonitrile, isoprene and styrene in the graft natural rubber are shown in Table 4.8. The details of all data are shown in Appendix D.

## 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 free SAN were calculated as shown in Figures 4.8. The ratios of acrylonitrile, isoprene and styrene monomers were calculated by using number of mole according to C, H, N and O in the graft natural rubber obtained from the analysis. Effect of reaction temperature on composition of graft natural rubber is shown in Table 4.8. The details of all data and calculations are shown in Appendix E.

The ratios of acrylonitrile and styrene in graft natural rubber was confirmed by the ratios of acrylonitrile and styrene monomers in the free SAN.

Figures 4.11 a and b show the effect of reaction temperature on the ratio of styrene and acrylonitrile in the graft 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 and reached the maximum value at 50 °C. At the reaction temperature above 50 °C, the acrylonitrile content decreased.

The interesting finding in this work is the technique for the determination of copolymer composition of graft natural rubber. Figure 4.10 and 4.11 show that the results of these two techniques are acceptable. The results confirm that the FTIR method and CHN\O method are suitable for this measurement.



**Table 4.7.** Effect of reaction temperature on the composition of free SAN.

Reaction Temperature (°C)	Acrylonitrile/Styrene	
	FTIR method	CHN\O method
30	49.7 : 50.3	39.9 : 60.1
40	31.5 : 68.5	28.0 : 72.0
50	43.7 : 56.3	39.9 : 60.2
65	28.7 : 71.3	27.6 : 72.4

**Table 4.8.** Effect of reaction temperature on the composition of graft natural rubber.

Reaction Temperature (°C)	Acrylonitrile/Isoprene/Styrene	
	FTIR method	CHN\O method
30	6.8 : 86.4 : 6.9	4.8 : 91.4 : 3.7
40	8.0 : 74.5 : 17.5	5.8 : 83.9 : 10.3
50	11.8 : 72.9 : 15.2	8.9 : 77.5 : 13.6
65	6.9 : 76.0 : 17.1	5.3 : 73.7 : 21.0

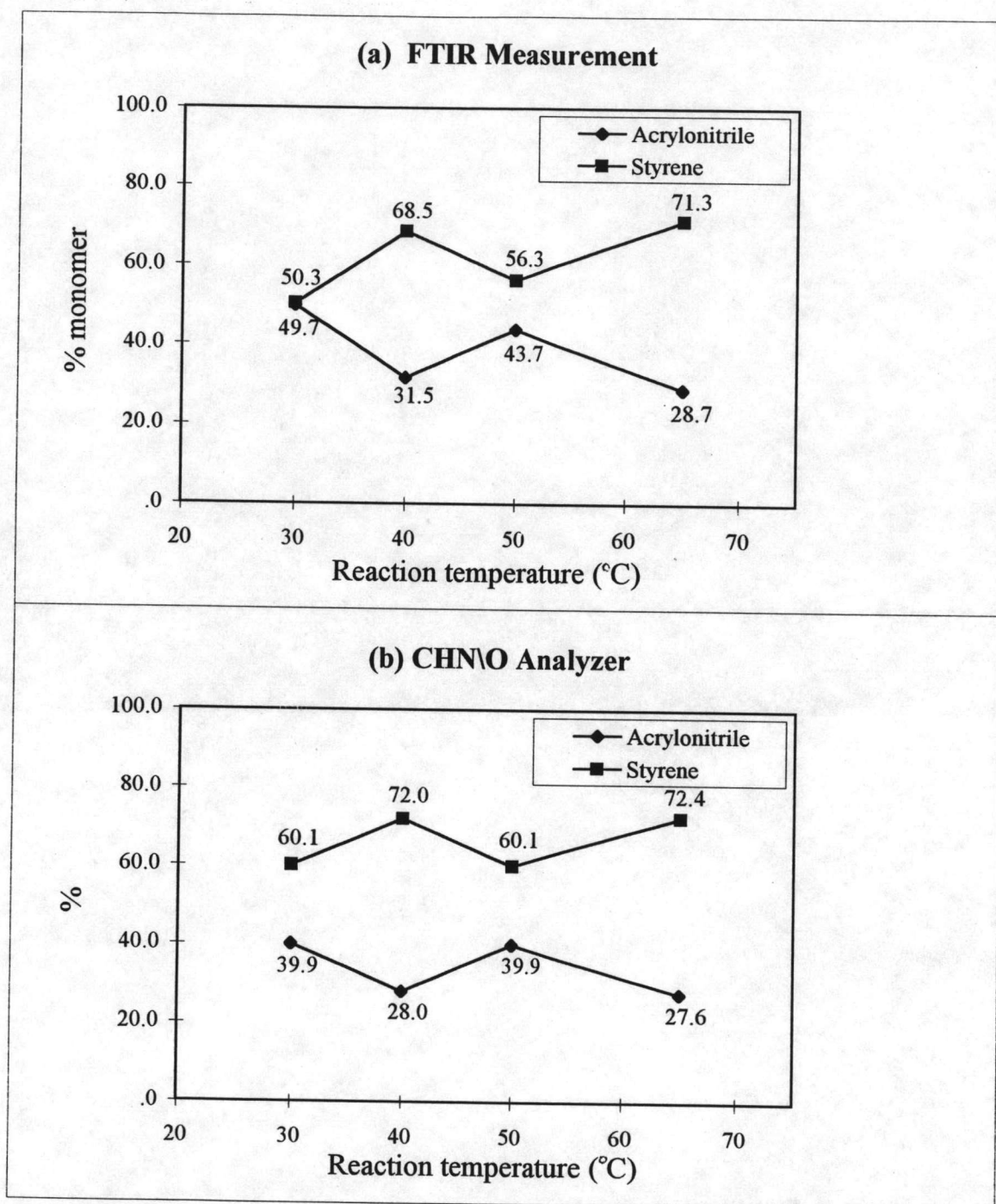
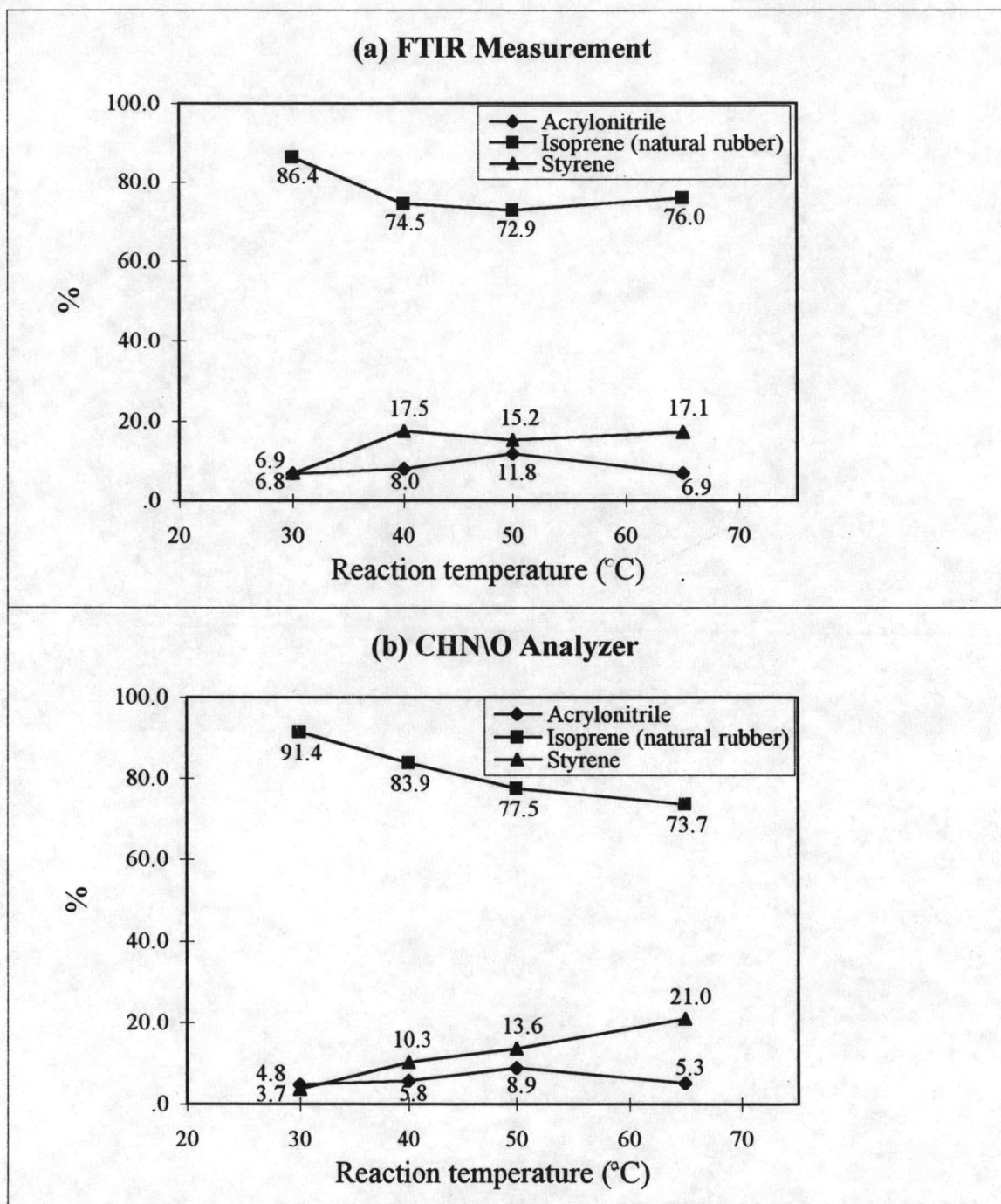


Figure 4.10. Effect of reaction temperature on the composition of free SAN.

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



**Figure 4.11.** Effect of reaction temperature on the composition of graft natural rubber.

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

### Thermal Properties of Graft Natural Rubber

It is known that the processing history of polymers reflect the thermal properties. The property which derived from the thermal data is the glass transition temperature  $T_g$  ( $^{\circ}\text{C}$ ). In this study, differential scanning calorimetry (DSC) was used to obtain the  $T_g$  of the graft natural rubber. Figures F.1-4 show the DSC thermogram of the graft natural rubber polymerized at various temperatures of 30, 40, 50, and 65  $^{\circ}\text{C}$ . The values of  $T_g$  derived from the DSC thermograms are shown in Table 4.9.

**Table 4.9.** The glass transition temperature ( $T_g$ ) of the graft natural rubber polymerized at various temperatures.

Reaction temperature ( $^{\circ}\text{C}$ )	Glass transition temperature ( $^{\circ}\text{C}$ )		
	Isoprene	Styrene	Acrylonitrile
30	-64.5	105.3	124.5
40	-63.7	101.1	125.2
50	-63.2	104.1	121.2
65	-63.2	105.1	124.9

At the reaction temperature of 50  $^{\circ}\text{C}$  for graft copolymerization, the strong endothermic effect was observed approximately about 100-130  $^{\circ}\text{C}$ . This was probably due to the high content of styrene and acrylonitrile in the samples and the peaks of  $T_g$  from 100 to 130  $^{\circ}\text{C}$  were exhibited. It was also shown that the copolymer product was random copolymer [25, 26].

## Thermoplastic Blends

### 1. Mechanical Properties of Thermoplastic Blends

For the preparation of a thermoplastic blends, the graft natural rubber was blended with SAN. The graft copolymerization of styrene and acrylonitrile on natural rubber latex was carried on at 50 °C for 8 hours. After the addition of 1.0 part of a phenolic antioxidant, the graft latex was coagulated, then washed and casted. Finally, the graft rubber sheet was dried at 50 °C in vacuum oven. The graft natural rubber was blended with SAN ( $\bar{M}_n = 35,450$ ,  $\bar{M}_w = 106,293$ ,  $\bar{M}_w/\bar{M}_n = 2.99$ ) 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.

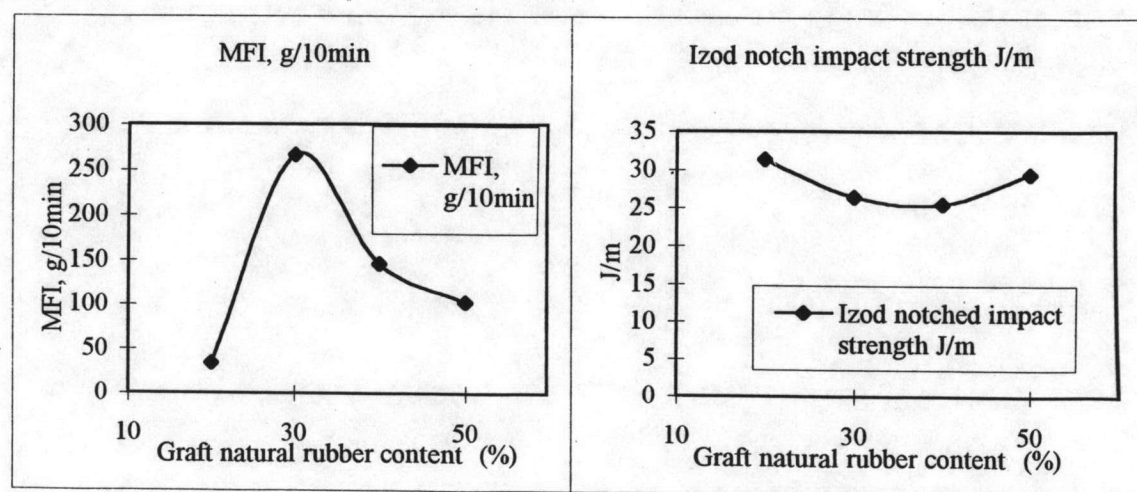
Table 4.10 and Figure 4.13 illustrate the effect of the graft natural rubber content on the mechanical properties. The mechanical properties decreased with increasing the graft natural rubber content. This effect may be attributed to the process of blending of graft natural rubber with SAN. The process of blending consisted of three steps. The first step was to blend the graft 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 at 200 °C. The third step was to obtain the standard bar and the sheet by injection molding at nozzle temperature 250 °C. Therefore, some portion of rubber was possibly degraded, because the color of the sample was observed at each step. The more graft natural rubber content, the lower the mechanical properties of the blends.

ABS GA703 and ABS QE1083 (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 4.10.** Effect of graft natural rubber content on the mechanical properties of the thermoplastic blends.

Property	Test method	Blending of graft NR : SAN				ABS	ABS
		20:80	30:70	40:60	50:50	GA703	QE1083
MFI, g/10min	D1238	34.1	267.0	146.0	103.0	50.0	27.0
Izod notched impact strength J/m	D256	31.4	26.5	25.5	29.4	122.5	117.6
Tensile strength, MPa	D634	44.7	23.4	16.3	8.8	45.4	45.0
Elongation at break (%)	D634	4.5	2.5	2.5	2.0	-	-
Flexural strength, MPa	D790	69.8	38.1	27.4	-	63.6	78.0
Flexural modulus, GPa	D790	2.66	1.18	1.47	-	2.2	2.8
Rockwell hardness, R-scale	D785	115.0	89.0	54.0	-	106.0	106.0
Heat distortion temp, °C	D648	87.2	86.2	78.6	70.6	86.0	87.0



**Figure 4.12.** Effect of graft natural rubber content on mechanical properties of thermoplastic blends



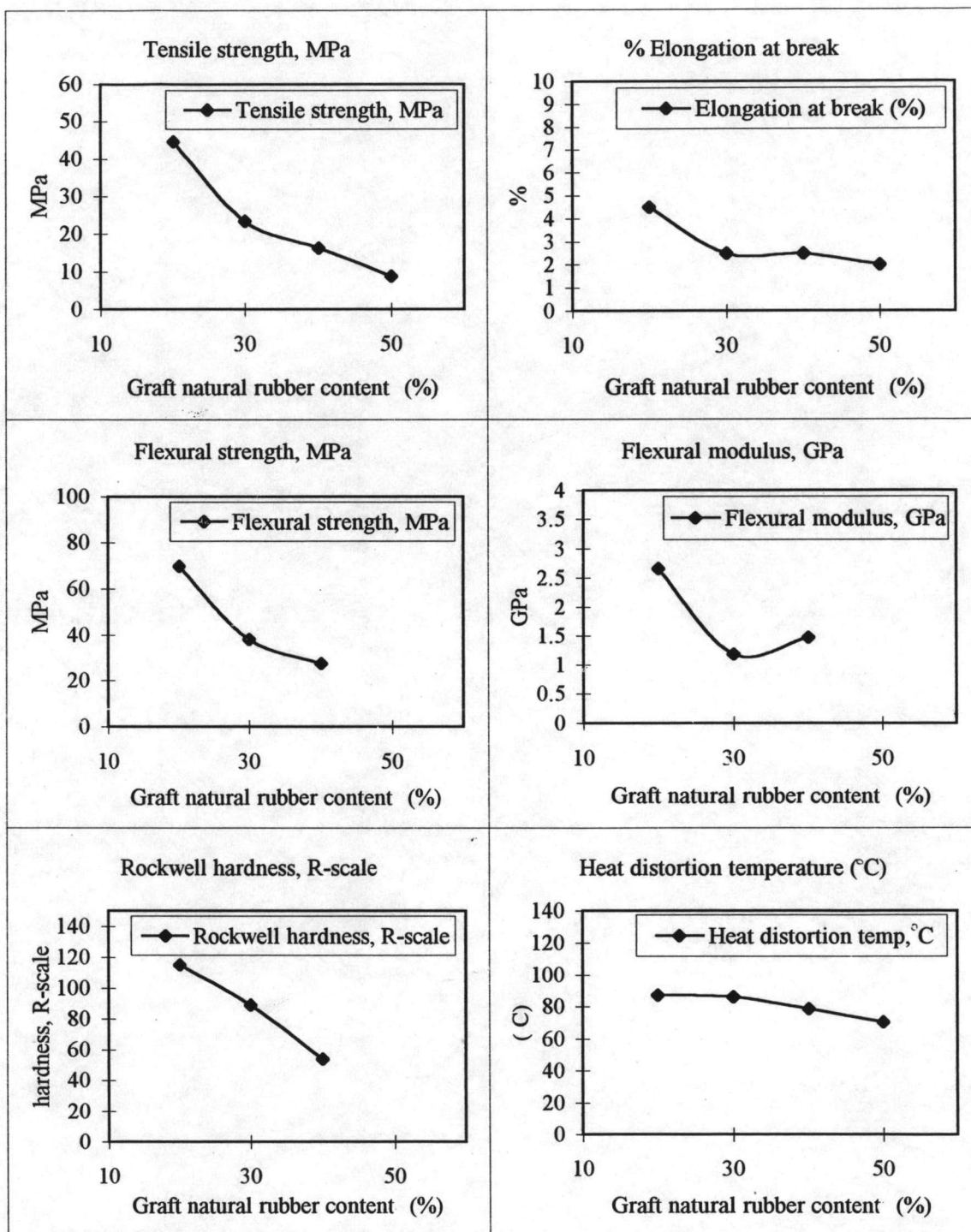


Figure 4.12. (continued)

## 2. Thermal Properties of Thermoplastic Blends

Figures 4.13-4.16 show the DSC thermogram of the thermoplastic blends at various contents of graft natural rubber. To observe the glass transition temperature of the blends, the temperature range was from -150 to 250 °C and the heating rate was 10 °C/min.

From the DSC thermograms of the blends, the strong endothermic effect increased with increasing the graft natural rubber content, this effect was observed from approximately from -80 to -50 °C. The effect was probably due to the high content of polyisoprene in the samples. The peak of  $T_g$  was observed in the range of 100-130 °C. It was also shown that the copolymer product was random copolymer [25, 26].



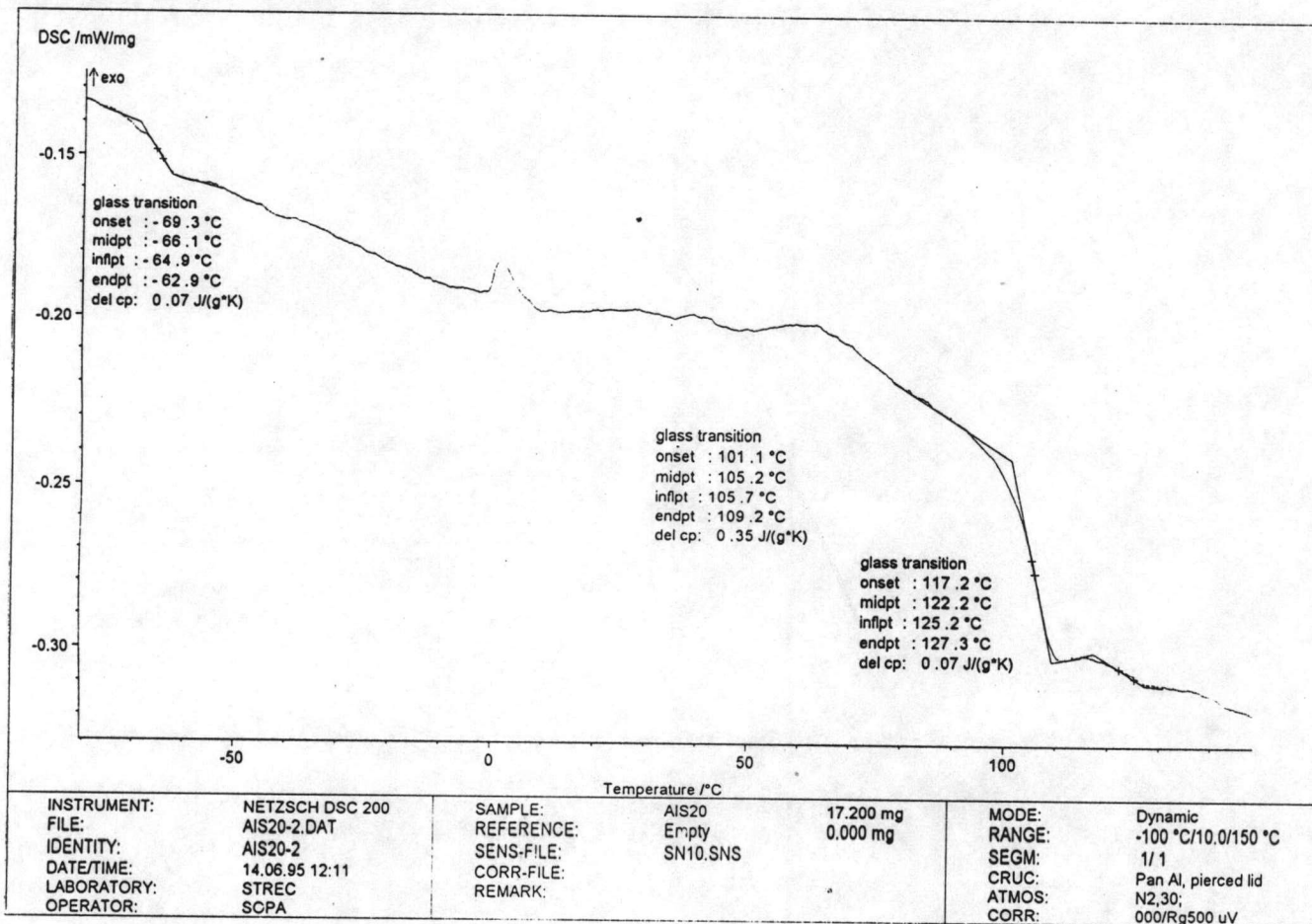


Figure 4.13. DSC thermogram of thermoplastic blend, 20 % of graft natural rubber.

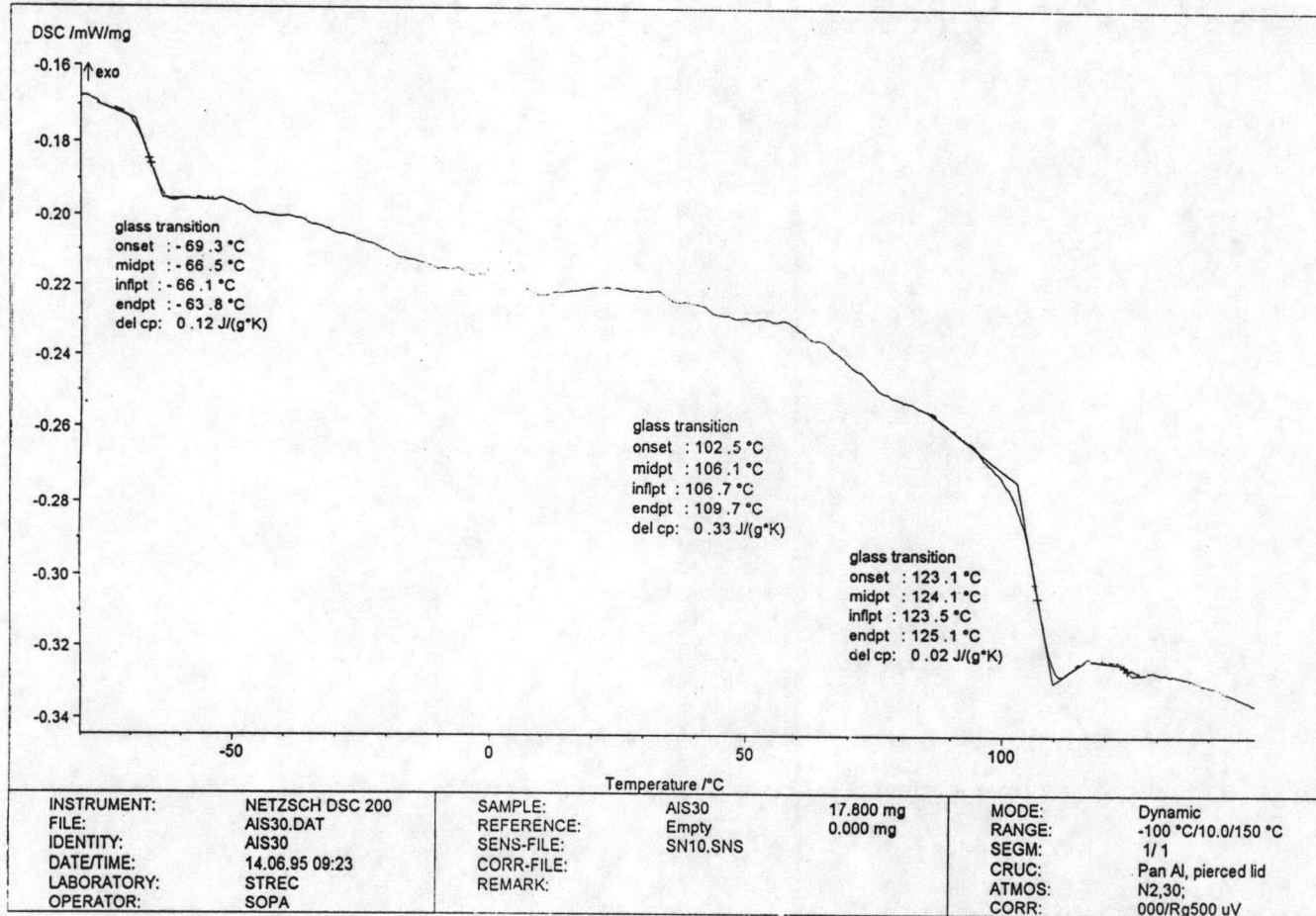


Figure 4.14. DSC thermogram of thermoplastic blend, 30 % of graft natural rubber.

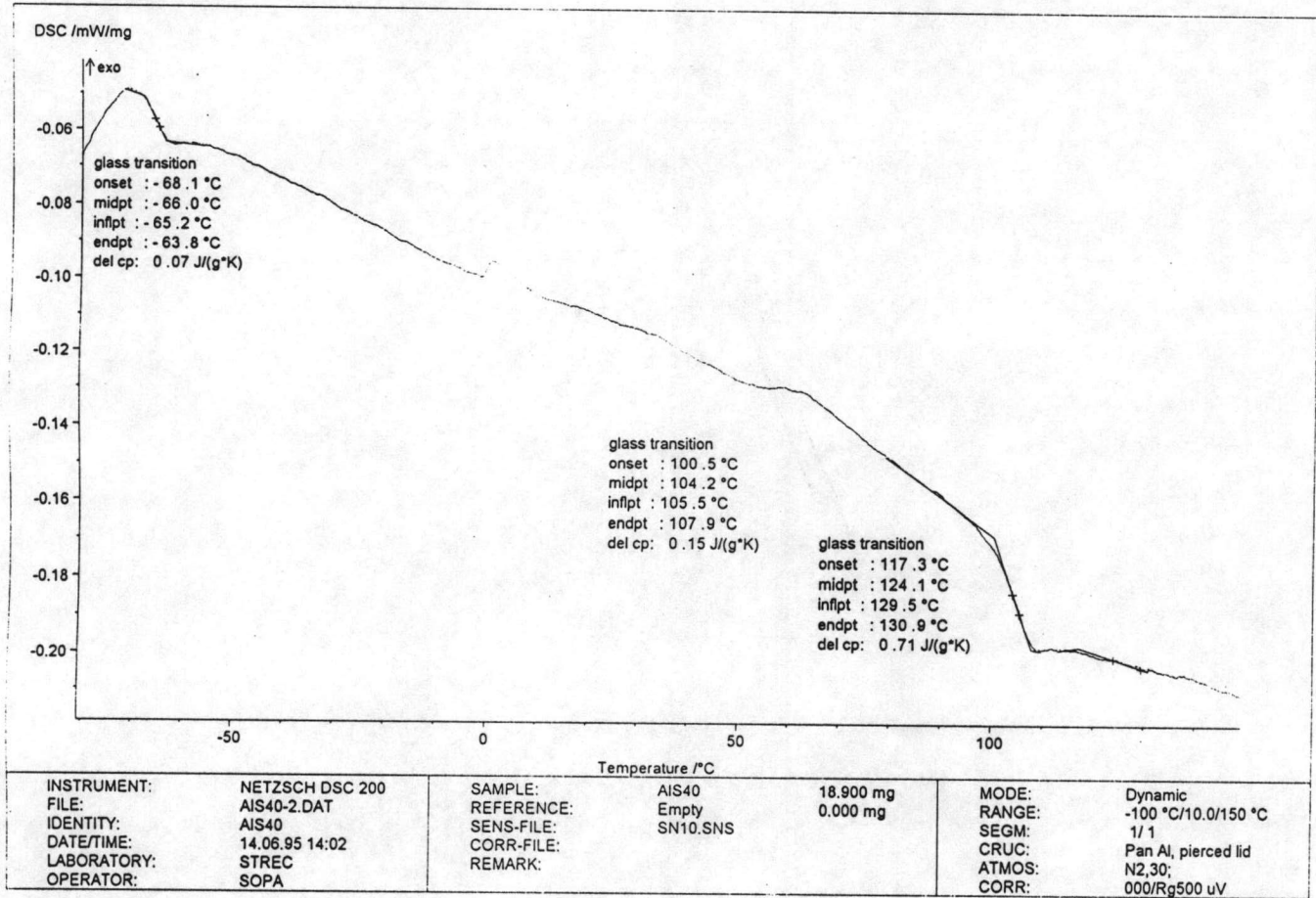


Figure 4.15. DSC thermogram of thermoplastic blend, 40 % of graft natural rubber.

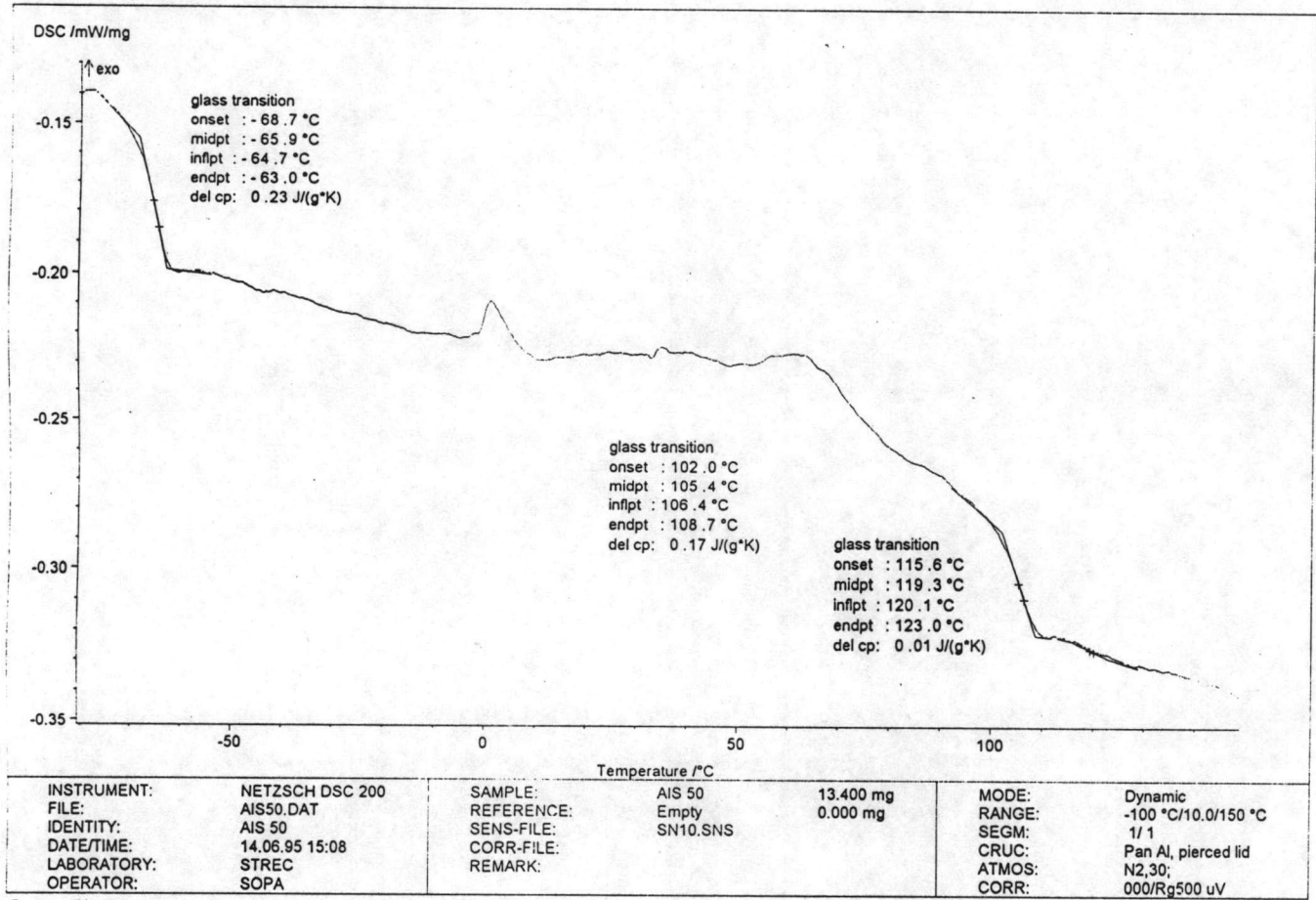


Figure 4.16. DSC thermogram of thermoplastic blend, 50 % of graft natural rubber.