

CHAPTER IV

RESULTS AND DISCUSSION

Chemical modification of natural rubber can be employed to alter the properties of natural rubber. The grafted natural rubber in the latex phase with MMA monomer was prepared by using the redox polymerization. The blends of grafted natural rubber and plasticized PVC were prepared by mechanical blending on two rolls mill and the physical properties of the blends were investigated.

4.1 Properties of Natural Rubber Latex

The natural rubber latex (HA) preserved with 0.7% ammonia solution was obtained from Thai Rubber Latex Corporation (Thailand) Public Co.,Ltd. The latex consisted of particles of rubber hydrocarbon and non-rubber constituents suspended in an aqueous serum phase. The average dry rubber content (DRC) and total solid content (TSC) of latex were 60.08 % and 62.52 % , respectively (average value from the experiment). The Mooney viscosity, ML(1+4)100°C and plasticity of dry natural rubber were 62.5 and 48.3, respectively. The properties of HA latex is shown in Table 4.1.

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

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), %	1.82
pH Value	10.48
KOH Number	0.51
Volatile Fatty Acid Number (VFA)	0.0205
Mechanical Stability Time @55% TSC, sec.	1,040
Specific Gravity at 25°C	0.9450
Magnesium Content (on solids), ppm	37
Chemical Stability Test (CST)	-ml
Remark: Free from Pentachlorophenol	

Source: Thai Rubber Latex Corporation (Thailand) Public Co.,Ltd. Bangplee Samutprakarn.

4.2 Preparation of Grafted Natural Rubber

The natural rubber latex (HA latex type), which preserved with 0.7% ammonia solution, was employed in the grafting emulsion polymerization process. In this study, t-butyl hydroperoxide and tetraethylene pentamine were used as redox initiation system. The t-butyl hydroperoxide was decomposed to free-radical, which could abstract a hydrogen atom from natural rubber backbone yielded the growing

rubber chain. Then, the growing rubber chain (or a rubber macroradical) could interacted with methyl methacrylate monomer to form graft copolymer.

In the study of the graft copolymerization of MMA monomer onto natural rubber latex, the appropriate conditions which yielded high percent conversion and high grafting efficiency (or percent graft copolymer) were obtained. The parameters investigated in this research work are as follows:

1. Effect of MMA content.
2. Effect of reaction temperature.
3. Effect of dry rubber content.
4. Effect of reaction time.

4.2.1 Effect of MMA Content

The preparation of grafted natural rubber was performed by emulsion polymerization process. In this case, the natural rubber latex were used as an seed latex of cis-1,4-polyisoprene, and methyl methacrylate monomer subsequently added to continue polymerization within the seed particle. NR latex particles were swollen with monomer, which was then grafted polymerized onto NR latex particles.

The reaction of NR latex of 30% dry rubber content (1000 g) with 0.9 g of t-butyl hydroperoxide and 3.5 g of 10% tetraethylene pentamine aqueous solution as a redox initiator was carried out at 30°C for 6 hr. The influence of monomer content on % graft yield and conversion is shown in Table 4.2 and Figure 4.1. It can be seen that the graft copolymer decreases with increasing MMA content. The reason is that the homopolymers is formed more readily than the graft copolymer. Figure 4.1 also shows the effect of MMA content on percentage free rubber and percentage free PMMA. It can be seen that, the PMMA homopolymer increases and free rubber decreases with increasing MMA monomer content. This mean that homopolymerization was preferred to graft copolymerization. The conversion

increases with increasing the MMA content up to 60 phr and with further increase of the MMA content the conversion decrease.

Table 4.2 Effect of MMA content on graft copolymerization: NR of 30% dry rubber content; temp = 30°C; time = 6 hr.

Grafting properties	MMA content, phr			
	20	40	60	80
% Graft copolymer	87.54	87.10	82.62	80.26
% Free rubber	9.34	7.66	7.17	4.94
% Free PMMA	3.12	5.24	10.20	14.81
% Conversion	75.4	77.4	81.5	77.6

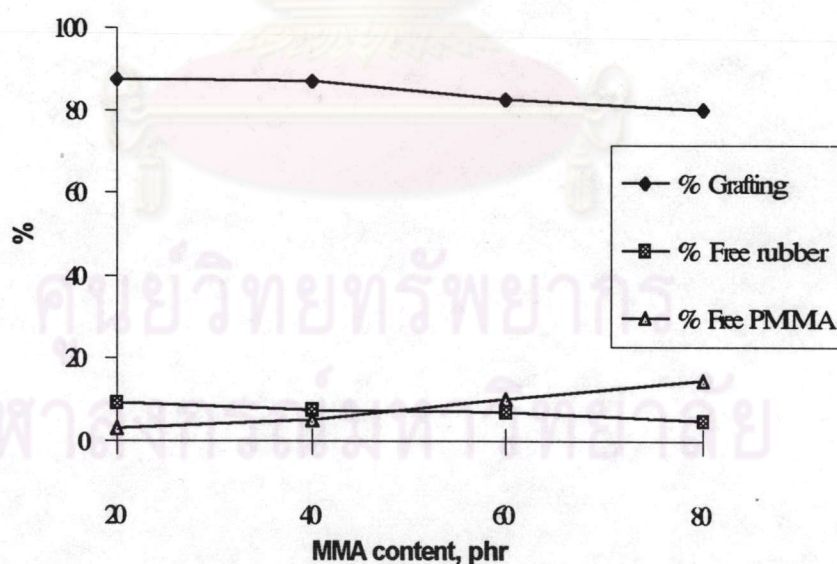


Figure 4.1 Effect of MMA content on graft characteristics of grafted natural rubber.

4.2.2 Effect of Reaction Temperature

The influence of temperature on graft copolymerization is shown in Table 4.3 and Figure 4.2, 4.3. With increasing temperature, decomposition of initiator increases, it results an increased number of free radicals and the rates of polymerization and grafting increase. But further increase in temperature increases mobility of these free radicals, and hence mutual termination takes place, this results the decreased availability of the free radicals for polymerization. The % graft copolymer increases very slightly with increasing temperature. The results indicate that with increasing temperature, the percentage of graft-on increases, which might be due to swellability of rubber, solubility of monomer and its high diffusion rate. The highest grafting efficiency was observed at the reaction temperature of 40°C.

Table 4.3 Effect of reaction temperature on graft copolymerization: NR of 30% dry rubber content; time = 6 hr.

Grafting properties	Reaction temperature, °C		
	30	40	50
- MMA = 20 phr			
% Graft copolymer	87.54	96.00	93.05
% Free rubber	9.34	3.61	2.67
% Free PMMA	3.12	0.39	4.28
% Conversion	75.4	77.4	93.5
- MMA = 40 phr			
% Graft copolymer	87.10	88.38	89.34
% Free rubber	7.65	8.29	8.28
% Free PMMA	5.25	3.33	2.38
% Conversion	81.0	86.0	84.1

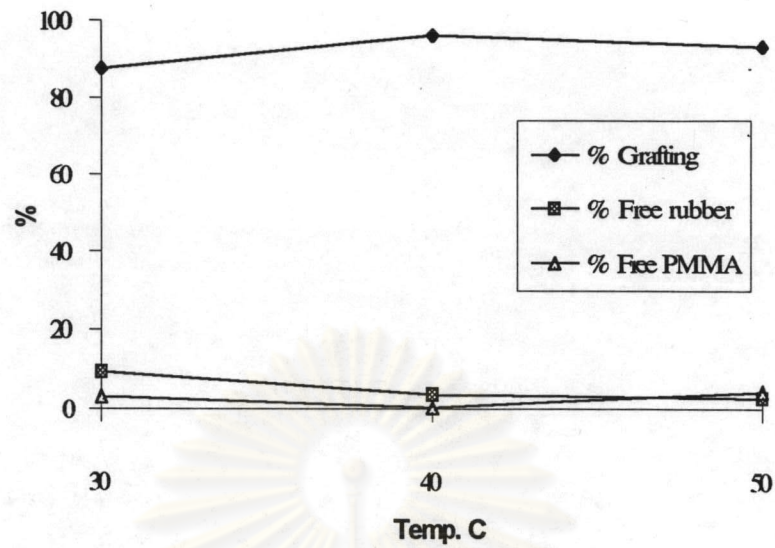


Figure 4.2 Effect of temperature on graft characteristics of grafted NR
 reaction time, 6 h; NR of dry rubber content, 30 %; MMA content,
 20 phr.

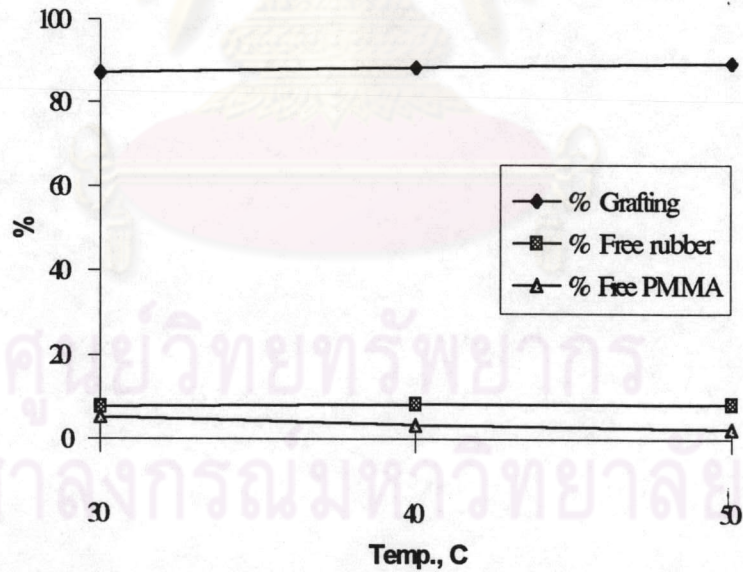


Figure 4.3 Effect of temperature on grafting characteristics of grafted NR:
 reaction time, 6 h; NR of dry rubber content, 30 %; MMA content,
 40 phr.

4.2.3 Effect of Latex Concentration

NR latex with different dilutions (from 30 to 50% dry rubber content by weight) was grafted copolymerized with 40 phr of MMA monomer at 30°C. The effect of latex concentration on graft copolymerization is shown in Table 4.4 and Figure 4.4. The percentage of graft copolymer decreases with latex concentration, but the percentage of free rubber and free PMMA increases with latex concentration. The % graft copolymer is highest at 30% dry rubber content. With increasing solid content, the latex showed a pronounced tendency to coagulate.

Table 4.4 Effect of latex concentration on the graft copolymerization. 40 phr of MMA; temp = 30°C; time = 6 hr.

Grafting properties	% dry rubber content		
	30	40	50
% Graft copolymer	87.10	85.78	77.08
% Free rubber	7.65	5.64	12.61
% Free PMMA	5.25	8.58	10.31
% Conversion	75.4	82.5	93.5

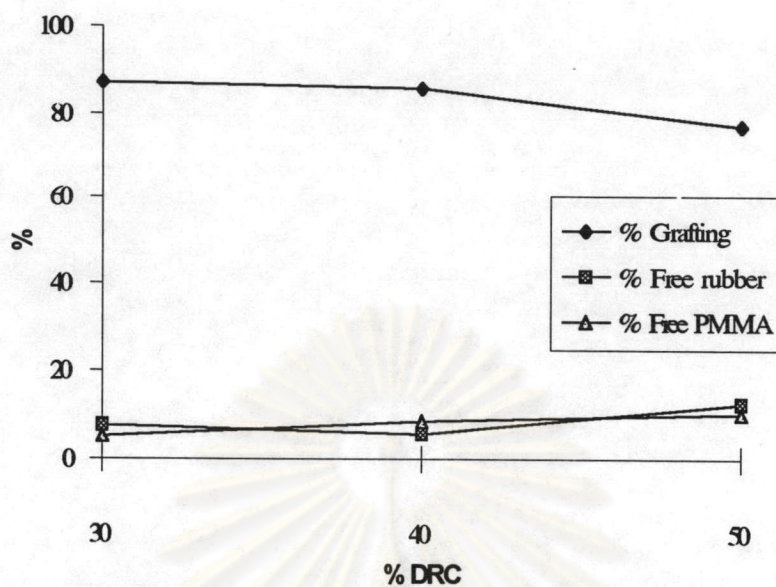


Figure 4.4 Effect of latex concentration on grafting characteristics of grafted NR.

4.2.4 Effect of Reaction Time

The effect of reaction time on the grafting of MMA onto NR are shown in Table 4.5 and Figure 4.5. the conversion increases with increasing reaction time.

Table 4.5 Effect of reaction time on the graft copolymerization: NR of 40% dry rubber content, 40 phr of MMA, temp = 30°C.

Reaction time, hr	% conversion
2	78.3
4	84.8
6	88.5
8	90.4

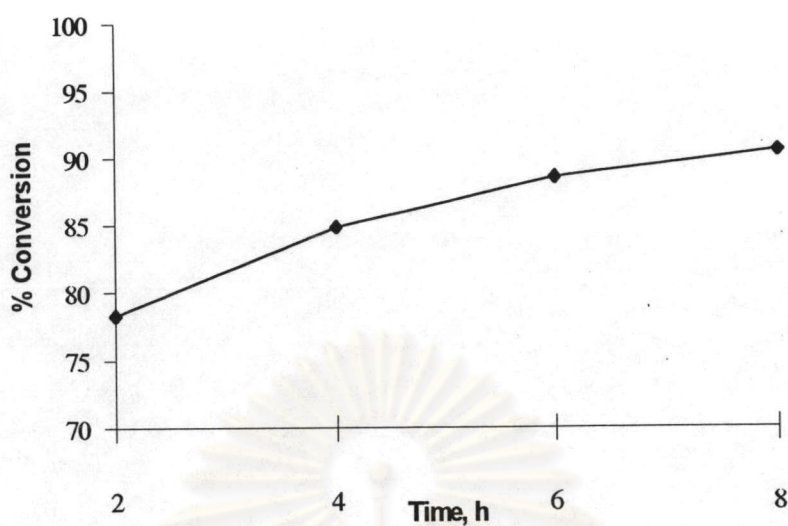


Figure 4.5 Effect of reaction time on percentage of conversion: NR conc., 30%; MMA content, 40 phr; temp., 30 °C.

4.3 Characterization of grafted natural rubber

4.3.1 FTIR Studies

Figure 4.6, 4.7, 4.8 and 4.9 show the infrared spectra in the region of 3500-500 cm^{-1} for natural rubber and grafted natural rubber (NR-g-MMA). The structure of NR-g-MMA was confirmed by FTIR measurement. The FTIR spectra of NR-g-MMA exhibited the characteristic absorption bands of C-H stretching vibration in aliphatic C-H bond at 2950 cm^{-1} and C=O stretching vibration at 1735 cm^{-1} and C=C stretching vibration at 1655 cm^{-1} . The new peaks in grafted NR appeared at 1735 cm^{-1} and 1148 cm^{-1} , due to carbonyl group (C=O stretching) which MMA was grafted on natural rubber backbone. Therefore, the carbonyl group of methyl methacrylate was introduced onto natural rubber. This confirms the occurrence of grafting. For the spectrum of natural rubber (Figure 4.6), no such peak was observed at 1735 cm^{-1} and 1148 cm^{-1} . The peak in Figure 4.6, 4.7 and 4.9 appeared at 2300 cm^{-1} , due to the noise which the FTIR spectrum was interrupted by unstable electric current.

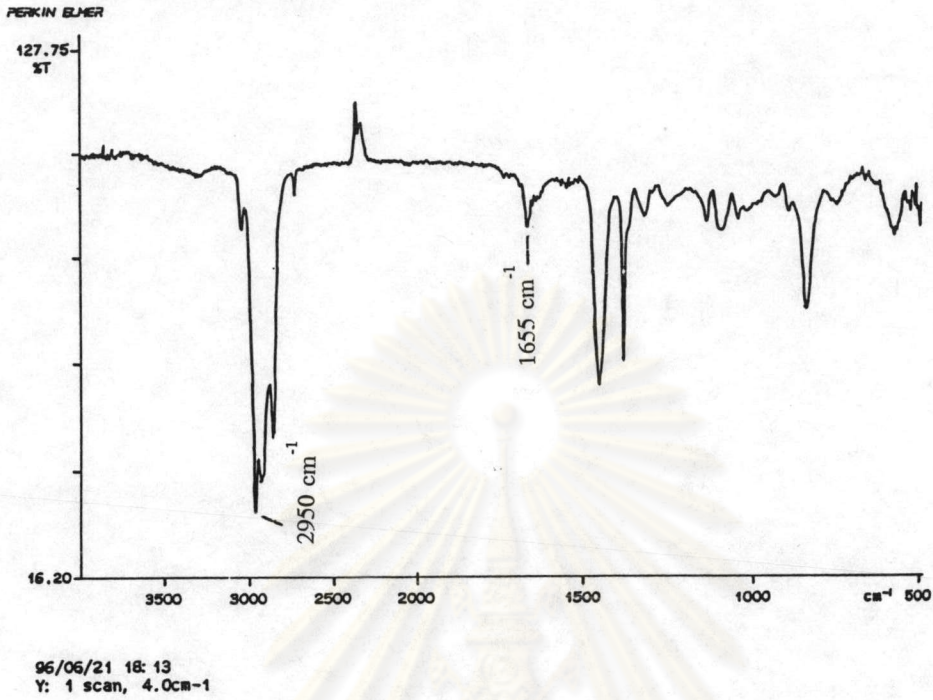


Figure 4.6 FTIR spectrum of Natural Rubber.

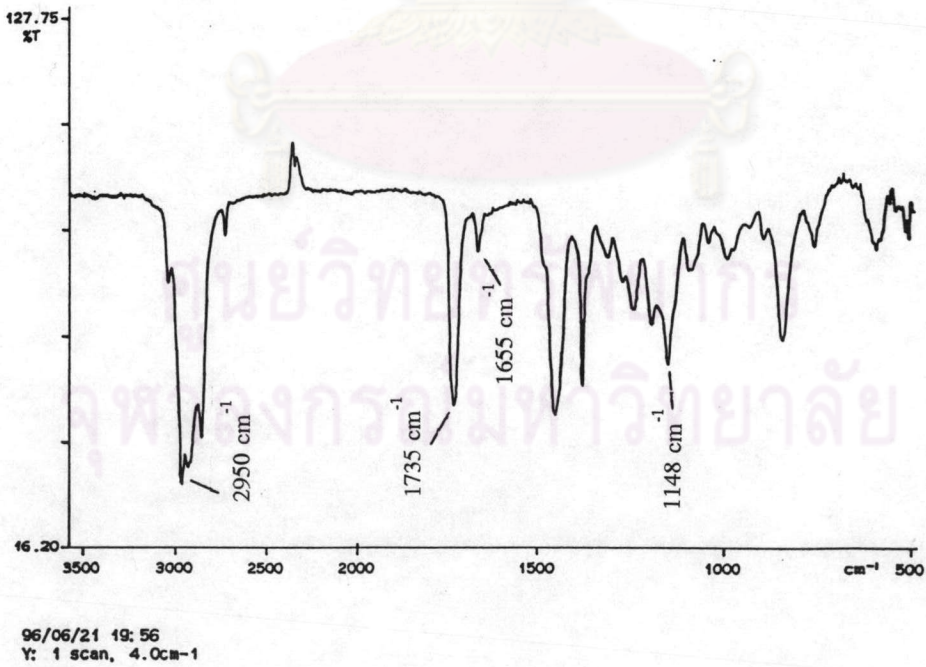


Figure 4.7 FTIR spectrum of NR-g-MMA (MMA = 20 phr)

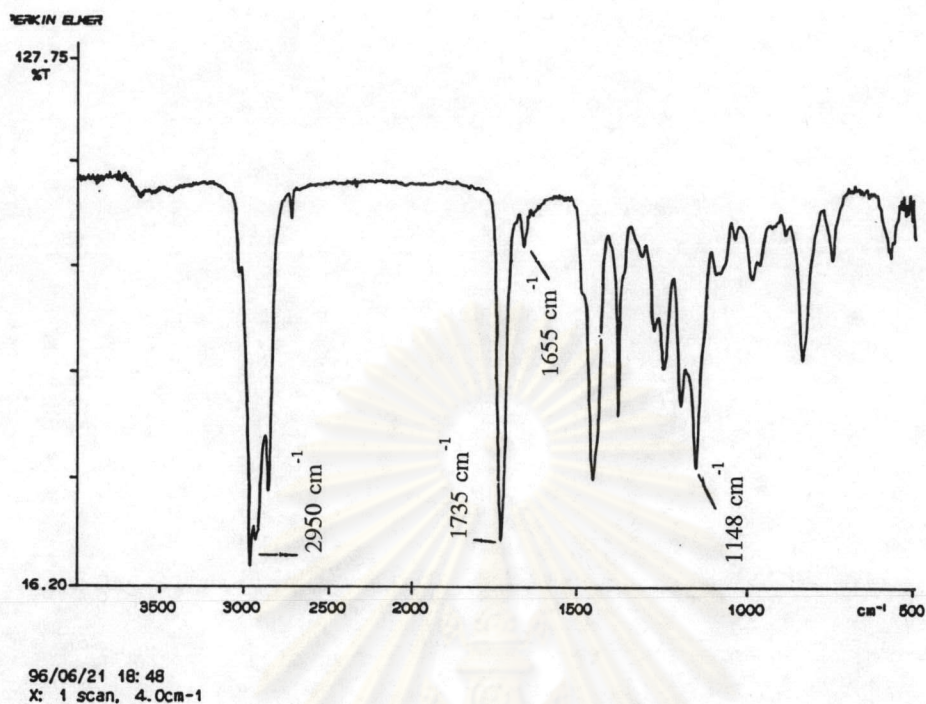


Figure 4.8 FTIR spectrum of NR-g-MMA (MMA = 40 phr)

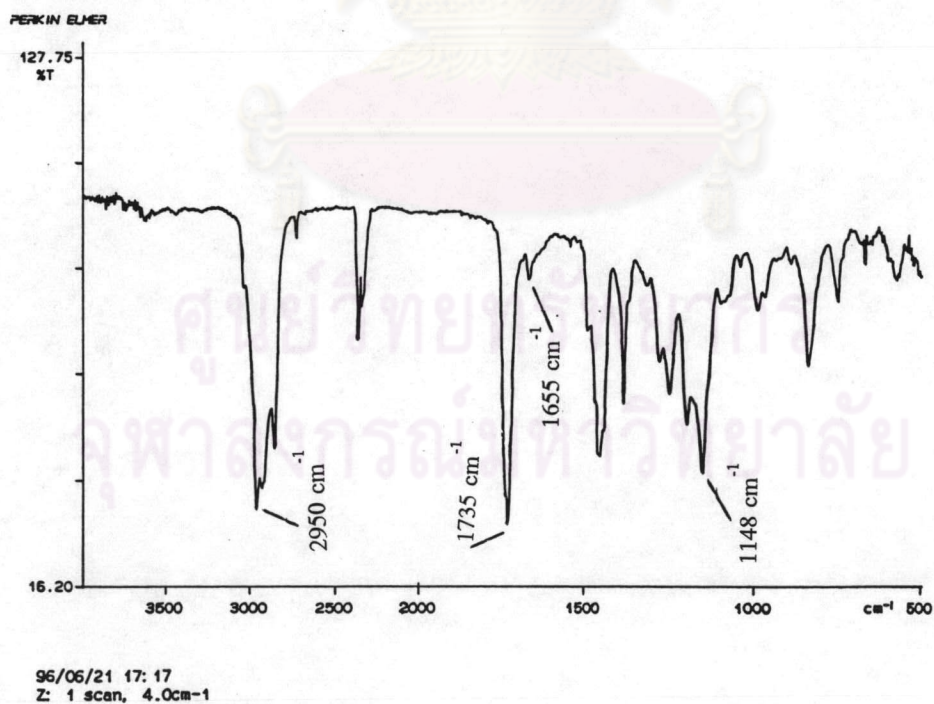


Figure 4.9 FTIR spectrum of NR-g-MMA (MMA = 60 phr)

4.3.2 Thermal analysis

Thermal properties of NR and all NR-g-MMA were determined by Differential Scanning Colorimetry (DSC) and Thermogravimetric (TG) analysis. Figure 4.10, 4.11, 4.12 and 4.13 show the TGA thermograms of NR and grafted NR. The heating rate was 10°C/min. and the temperatures of degradation in oxygen atmosphere were in the range 370-390°C. In general, all NR and NR-g-MMA exhibited good thermal stability with no significant weight loss up to temperature of approximately 350°C. Figure 4.14 and 4.15 show the DSC thermograms of NR and grafted NR, the deflection between -64°C to -65°C (T_g app. -64 and -65°C) was observed, which was due to the glass transition of NR. From Figure 4.15, a very small deflection (too faint) was observed due to the glass transition of PMMA component in the sample.

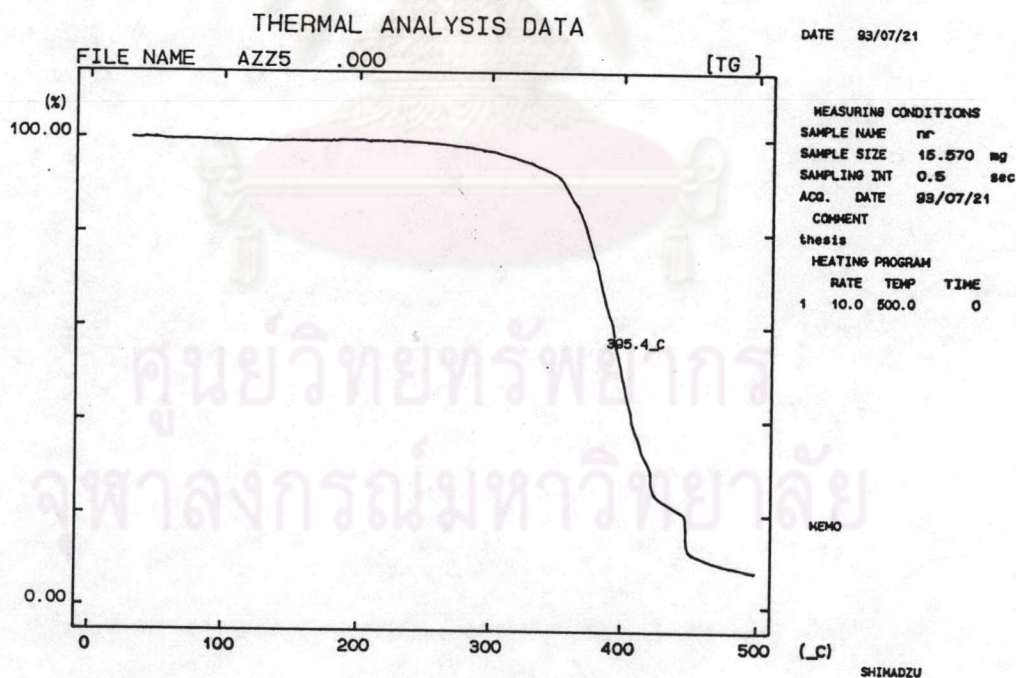


Figure 4.10 TGA thermogram of Natural Rubber.

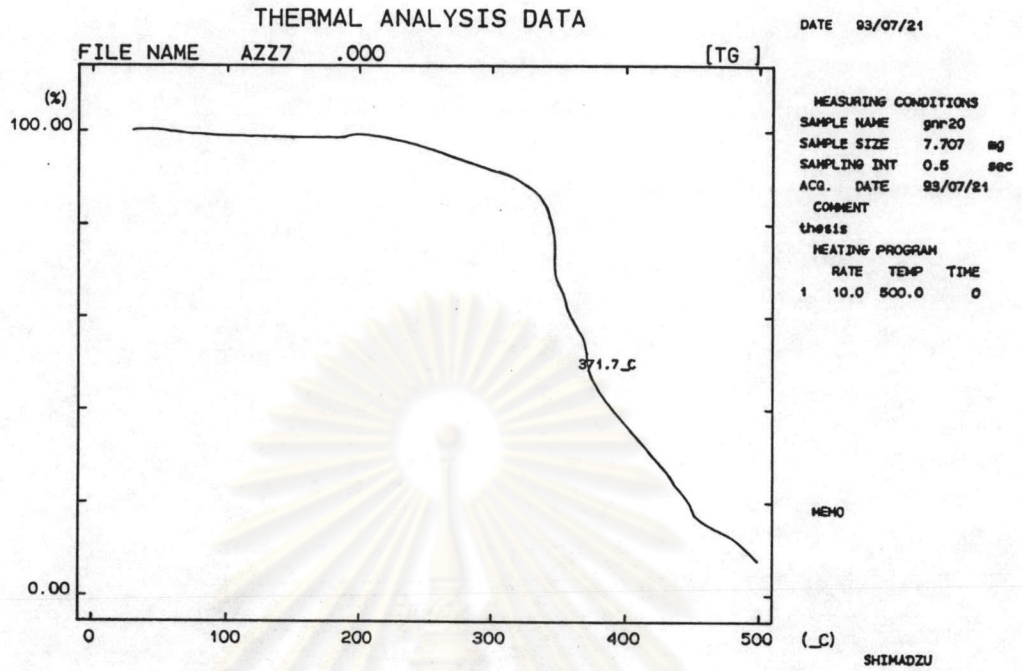


Figure 4.11 TGA thermogram of NR-g-MMA (MMA = 20 phr).

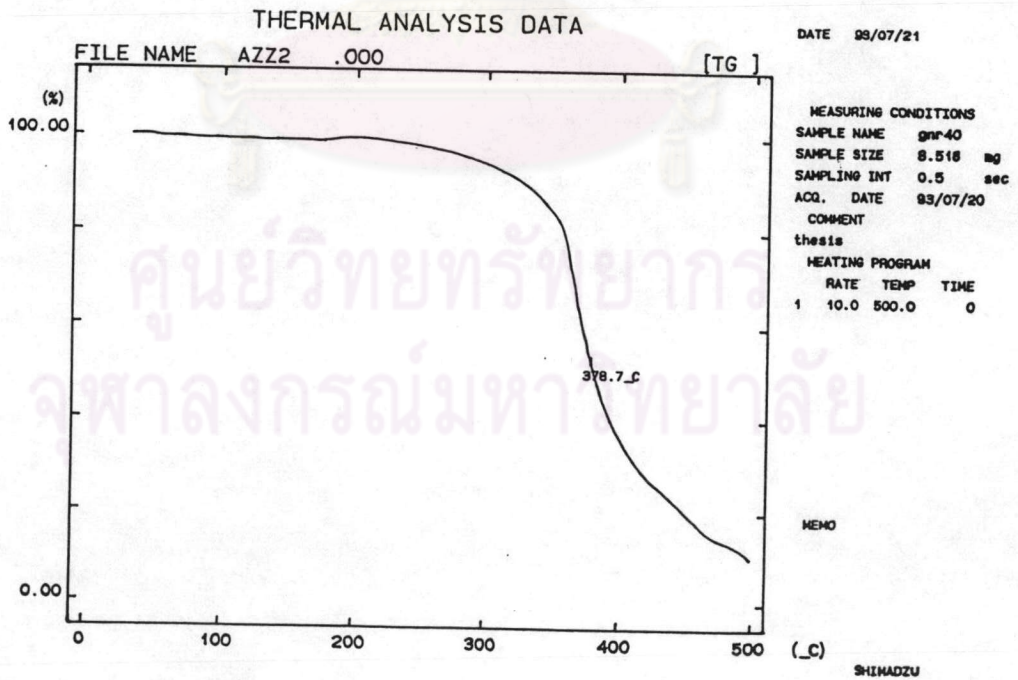


Figure 4.12 TGA thermogram of of NR-g-MMA (MMA = 40 phr).

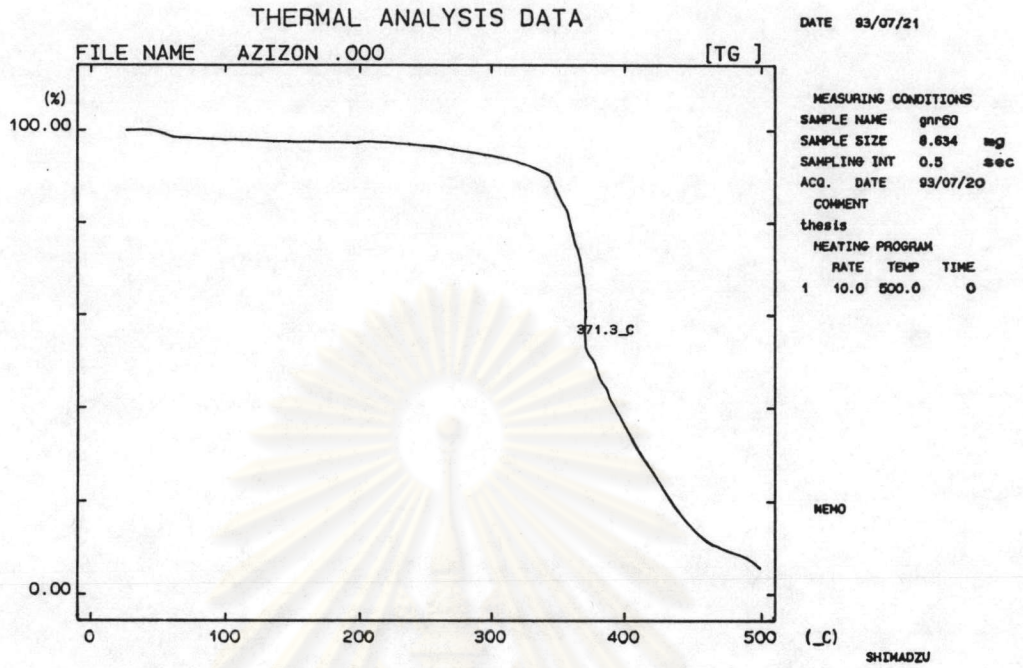


Figure 4.13 TGA thermogram of of NR-g-MMA (MMA = 60 phr).

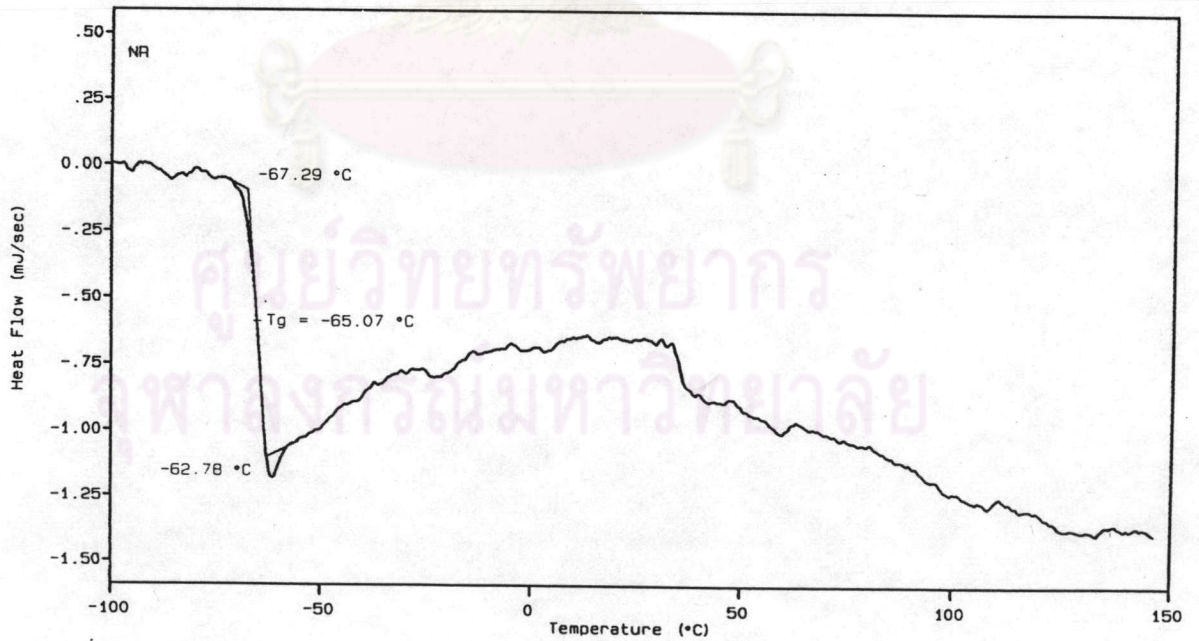


Figure 4.14 DSC thermogram of Natural Rubber.

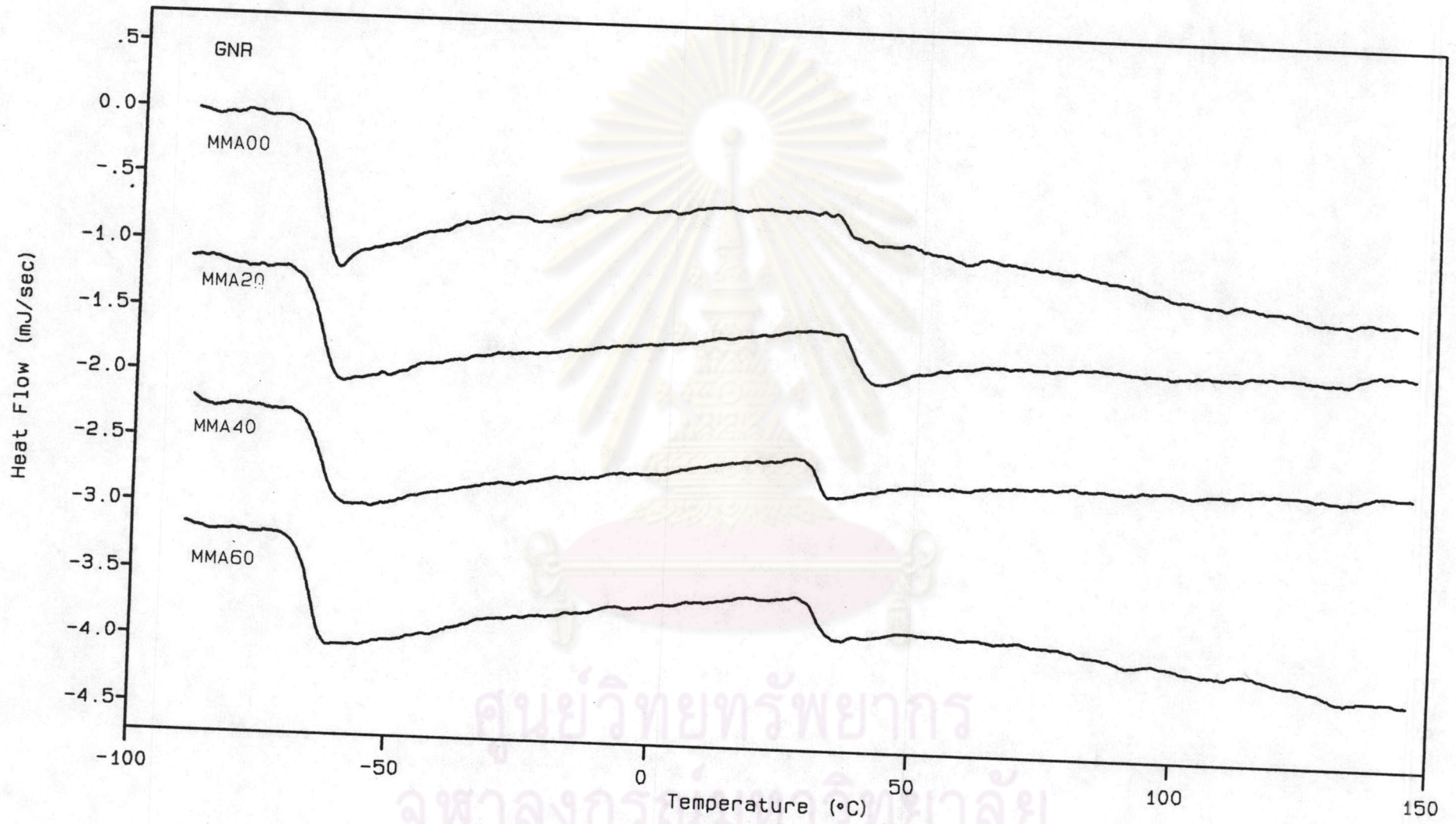


Figure 4.15 DSC thermogram of Natural Rubber and Grafted NR.

4.4 Rheometric Studies

The color of natural rubber solid was yellow. For the grafted NR, the yellow color disappeared when the MMA monomer content increased. During processing, the grafted NR product behaved essentially like natural rubber. The band was easily formed in the two-roll mill and the incorporation of the curatives was easy in these product. However, the band of grafted NR with higher MMA content was also processed more easily in two-roll mill. (not above 60 phr). Grafted natural rubber can be crosslinked by using any of the standard sulfur formulation normally employed for NR.

Monsanto rheographs of the grafted NR compounds at different MMA content are shown in Figure 4.16. The progressive formation of a crosslinked network in the system is manifested in the gradual rise in the torque with curing time. Table 4.6 and Figure 4.17, 4.18 summarize the effect of MMA content in rubber compounds on cure characteristics and physical properties. On the basis of maximum torque values (MH) of the the four different grafted NR, the degree of crosslinking increases in the following order:

$$\text{GNR-60} > \text{GNR-40} > \text{GNR-20} > \text{NR.}$$

But this crosslinking property tended to increase a little when MMA content was greater than 40 phr. The order of scorch time follows the sequence:

$$\text{GNR-60} > \text{GNR-40} > \text{GNR-20} > \text{NR.}$$

The main effect of MMA content was to increase the scorch delay and hence enlarge the cure time.

From Figure 4.19 and 4.20 show the physical properties of the different grafted NR. The tensile strength of grafted NR increased with increasing MMA content up to 40 phr and with further increases of MMA content, the tensile

strength decrease. The elongation at break decreased with increasing MMA content.

An optimum concentration of MMA to give NR-g-MMA with the highest tensile strength was found to be around 40 phr. This can be explained that there was poor adhesion between rubber particles, especially when MMA content was above 40 phr. The minimum torque (ML), maximum torque (MH), 300% modulus tear strength and hardness increased as the percentage of MMA content added into the NR latex increased. The increase of MMA concentration may cause the increase of the hard segment of MMA grafted chain and PMMA homopolymer.

Table 4.6 Cure characteristics and physical properties of different grafted NR compounds.

Properties	grafted NR Compound			
	NR	GNR-20	GNR-40	GNR-60
1. Cure characteristics				
ML, lb-in.	3.96	6.15	6.94	7.67
MH, lb-in.	18.70	20.23	23.46	23.69
Cure rate Index	82.21	90.09	74.63	49.50
Scorch time, min.	0.70	1.44	1.85	2.86
Cure time, min	1.86	2.55	3.19	4.88
2. Physical properties				
300% Modulus, MPa	2.11	4.43	16.00	18.87
T.S., MPa	24.86	27.68	31.37	27.68
E.B., %	780	680	530	329
Hardness, IRHD	27.00	31.60	72.17	95.83
Tear strength, N/mm	33.51	41.43	60.37	77.71

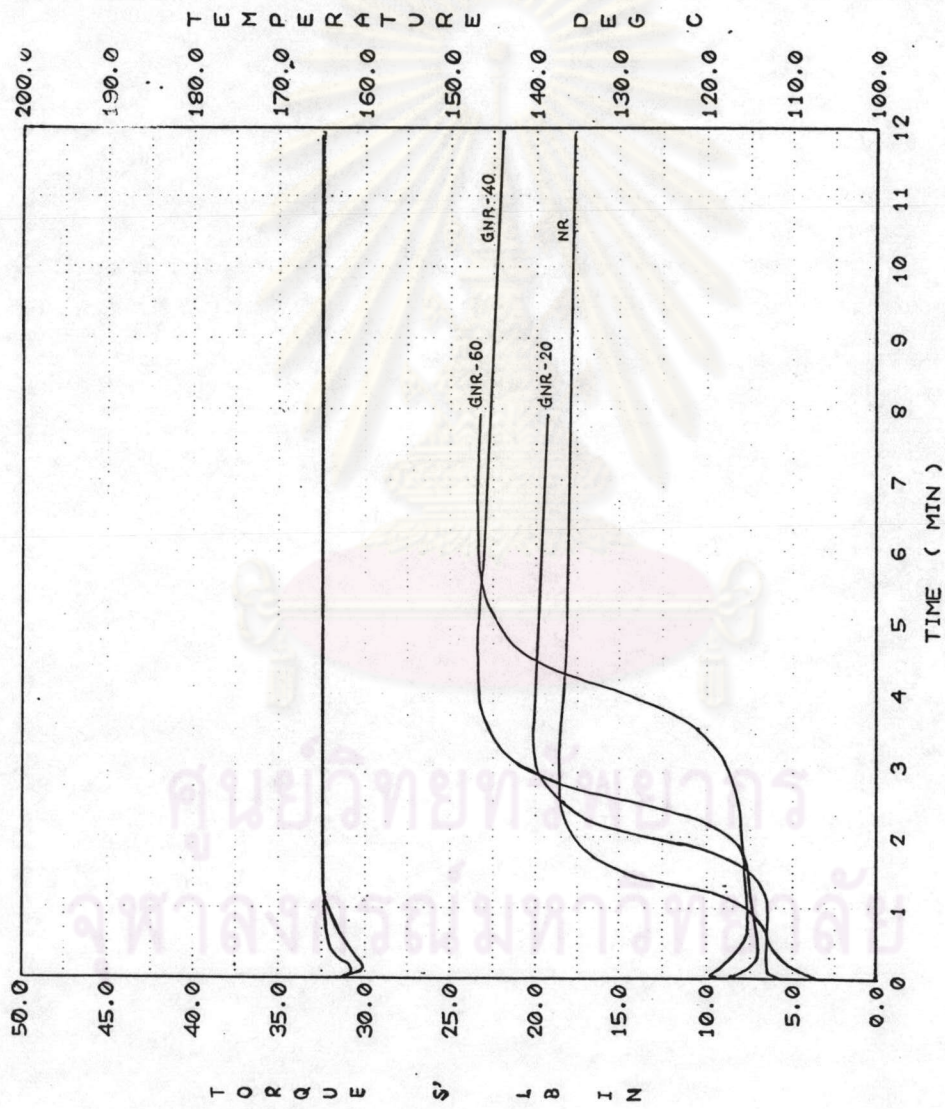


Figure 4.16 Monsanto rheographs of rubber compounds at 165°C.

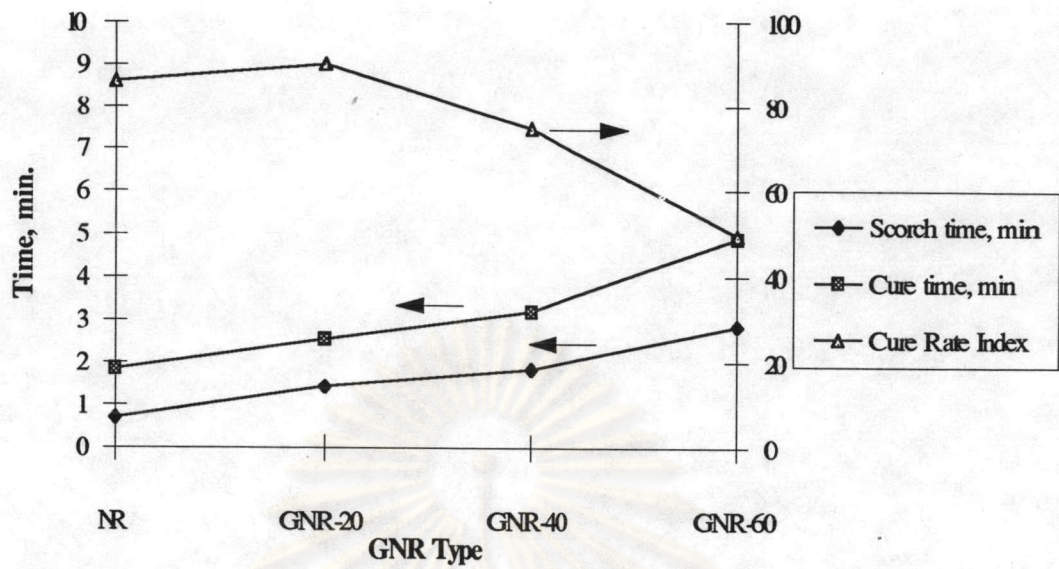


Figure 4.17 Effect of MMA content on cure characteristics of rubber compounds.

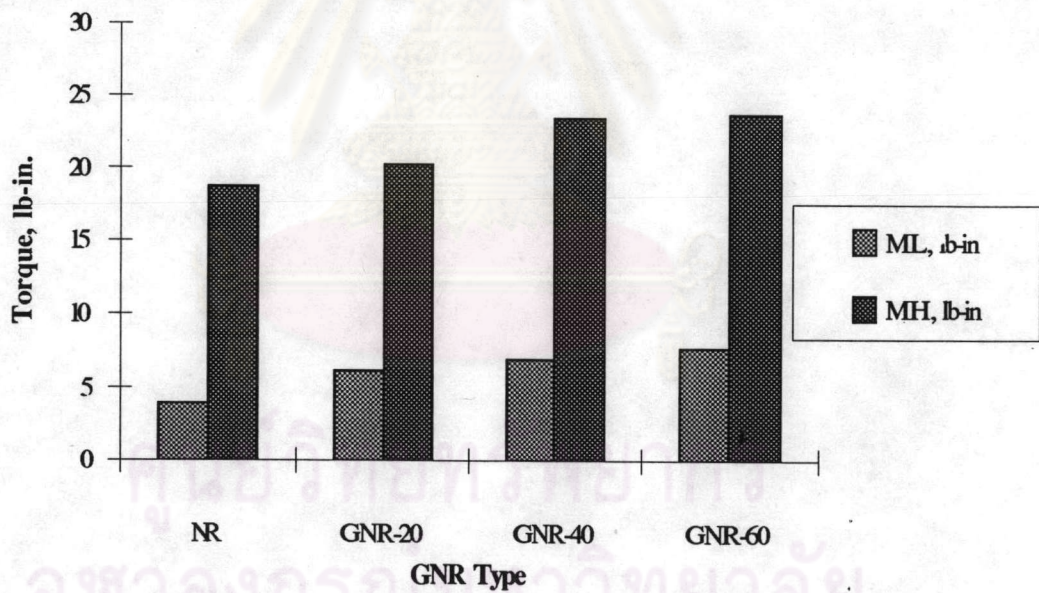


Figure 4.18 Effect of MMA content on ML and MH of rubber compounds.

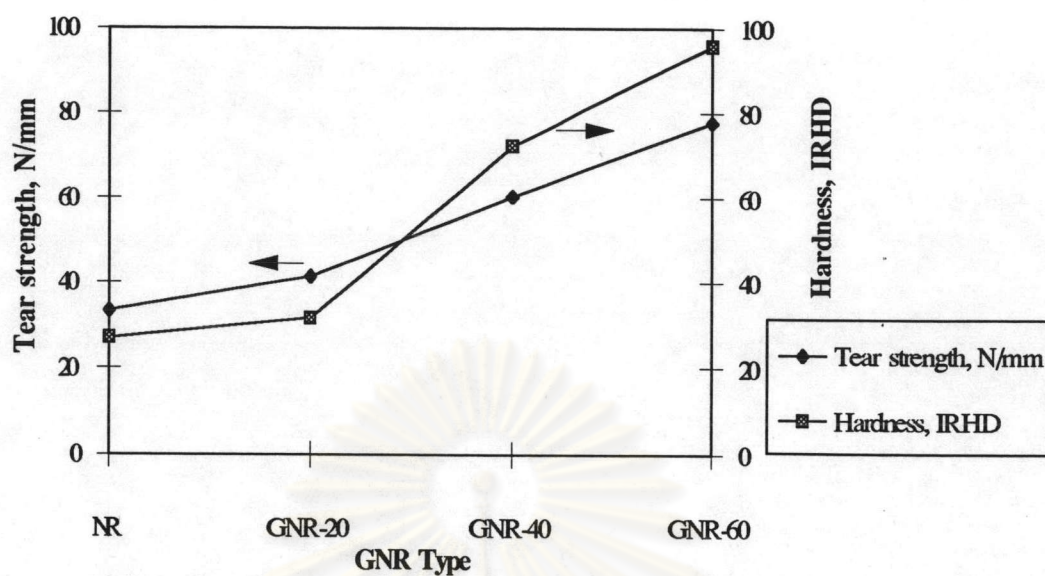


Figure 4.19 Effect of MMA content on tear strength and hardness of rubber compounds.

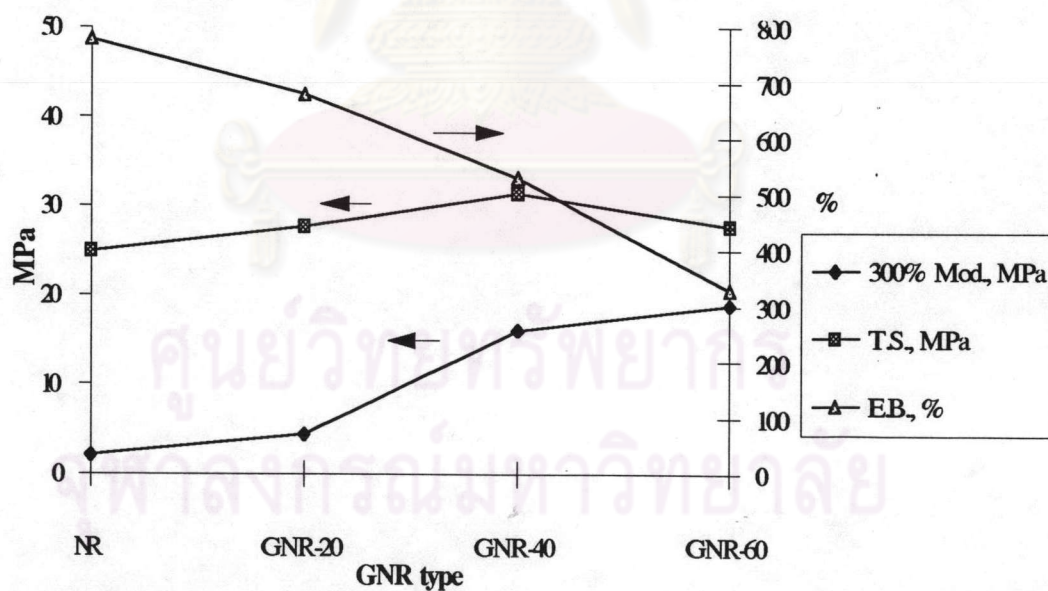


Figure 4.20 Effect of MMA content on physical properties of rubber compounds.

4.5 Properties of GNR/PVC blends

Effects of GNR/PVC blends compositions on the mechanical properties were investigated. The values of tensile strength, elongation at break and 300% modulus, are shown in Table 4.7 (a, b), 4.8 (a, b), 4.9 (a, b) and in Figure 4.21-4.25.

4.5.1 Tensile Properties

Tensile strength

From Figure 4.21a, the tensile strength of vulcanized blends increased with increasing level of MMA content in grafted NR. The GNR/PVC-P00 blends, especially NR and GNR20, had lower values than the other blends, due to the different viscosity between rubber and PVC-P00. For grafted rubber with MMA higher than 40 phr, the tensile strength was higher, due to the similar values of the viscosity of grafted NR and PVC. The other reason was the GNR had sufficiently the MMA content, which it could be miscible with PVC phase. For GNR/PVC blends of vulcanized rubber at high rubber content, the tensile strength was high compared with NR/PVC blends. From Figure 4.22a and 4.23a, both plasticized PVC (PVC-P20 and PVC-P40) deteriorate the tensile strength of blends.

Tensile strength increase with increasing rubber content. This can be explained that there was increased the crosslink density in rubber component at high rubber content. Because the PVC particles disperse in vulcanized rubber matrix phase (rubbery phase) due to static vulcanization, consequently, at high PVC content, the reverse phase can occur, thus vulcanized rubber phase disperses in PVC matrix (plastic phase). A minimum in tensile strength of the vulcanized system appeared at GNR/PVC-P20, GNR/PVC-P40 ratio of 40/60. This is comprehensible on the ground of change in morphology with composition. In regions where GNR or PVC predominated, there appeared finer dispersion and

better adhesion between the phases; the tensile strength that was dictated by the major component deteriorated on increasing the minor component. In region where no one component prevailed (GNR/PVC ratio of 60/40 to 40/60), both components existed in continuous phases, which would give rise to inferior tensile strength.

However, the tensile strength of GNR compounds increased with increasing rubber content for all range of GNR/PVC blends.

Elongation at break

From Figure 4.21b, the elongation at break of GNR/PVC (80/20 ratio) blends decreased with increasing MMA content in grafted NR, due to the presence of the plastic component. The elongation at break increases in the following order:

$$\text{PVC-P20} > \text{PVC-P40} > \text{PVC-P00}.$$

From Figure 4.22b, 4.23b, the elongation at break decreased with increasing PVC content. For the percentage of PVC-P20 in GNR/PVC-P20 above 40%, the elongation at break decreased rapidly. For GNR/PVC-P40, the elongation at break decreased rapidly when PVC-40 in blends was above 20%. From these results, It can be explained that the blends had changed in morphology. The minimum elongation at break of the vulcanized system were GNR/PVC of 40/60 for the blend, due to the higher thermoplastic (PVC, PMMA) content in the compound. Generally, PVC and PMMA was brittle thermoplastic (low elongation at break). Rubber component in GNR, improved this property of PVC component.

300% Modulus

From Figure 4.24, 4.25, for GNR/PVC compounds, the 300% modulus of polymer blends increases with decreasing GNR/PVC ratio because PVC compounds were characterized to be self-reinforcing in polymer blends. The 300% modulus of GNR/PVC blends increased with increasing MMA content in GNR type. At the same GNR/PVC ratio (all PVC content), 300% modulus increase in the following order: GNR-60/PVC > GNR-40/PVC > GNR-20/PVC > NR/PVC.

Table 4.7a Properties of NR/PVC-P00 and GNR20/PVC-P00 Blends.

Property	Blend NR:PVC				Blend GNR20:PVC			
	90:10	80:20	60:40	40:60	90:10	80:20	60:40	40:60
Tensile strength, MPa	10.95	6.81	NA	NA	7.82	7.15	5.59	NA
E.B., %	628	520	NA	NA	651	635	490	NA
300% Mod., MPa	2.13	1.52	NA	NA	2.00	2.28	3.50	NA
Tear strength, N/mm	28.84	25.26	NA	NA	41.12	39.40	32.39	NA
Hardness, IRHD	39.92	43.40	NA	NA	47.84	50.90	67.48	NA
Abrasion resistance, Taber type. NA cm ³ /2000 cycle.	NA	NA	NA	NA	NA	0.3078	0.3169	NA

Table 4.7b Properties of GNR40/PVC-P00 and GNR60/PVC-P00 Blends.

Property	Blend GNR40:PVC				Blend GNR60:PVC			
	90:10	80:20	60:40	40:60	90:10	80:20	60:40	40:60
Tensile strength, MPa	16.14	11.68	9.80	9.23	14.01	16.82	15.75	14.66
E.B., %	448	225	101	28	322	178	74	31
300% Mod., MPa	14.11	NA	NA	NA	13.42	NA	NA	NA
Tear strength, N/mm	44.29	38.86	42.60	38.23	52.11	56.09	47.44	47.73
Hardness, IRHD	62.26	65.88	82.92	98.04	95.14	96.02	97.58	99.54
Abrasion resistance, Taber type cm ³ /2000 cycle.	0.0048	0.0251	0.2335	0.2762	0.1617	0.2105	0.2722	0.2766

Table 4.8a Properties of NR/PVC-P20 and GNR20/PVC-P20 Blends.

Property	Blend NR:PVC-P20				Blend GNR20:PVC-P20			
	90:10	80:20	60:40	40:60	90:10	80:20	60:40	40:60
Tensile strength, MPa	16.12	15.86	11.41	4.04	20.08	22.63	16.74	12.51
E.B., %	820	711	589	53	618	583	304	154
300% Mod., MPa	1.93	3.03	3.73	NA	5.61	9.94	16.59	NA
Tear strength, N/mm	30.00	28.84	28.21	34.15	38.69	47.10	35.05	30.49
Hardness, IRHD	37.36	44.86	65.20	97.06	44.62	49.88	67.28	83.02
Abrasion resistance, Taber type cm ³ /2000 cycle.	NA	0.9356	1.4811	0.7656	NA	0.2171	0.2658	0.5136

Figure 4.8b Properties of GNR40/PVC-P20 and GNR60/PVC-P20 Blends.

Property	Blend GNR40:PVC-P20				Blend GNR60:PVC-P20			
	90:10	80:20	60:40	40:60	90:10	80:20	60:40	40:60
Tensile strength, MPa	22.51	22.60	17.37	16.81	21.80	22.01	19.15	20.54
E.B., %	453	322	177	80	311	323	182	109
300% Mod., MPa	14.86	20.73	NA	NA	18.98	20.88	NA	NA
Tear strength, N/mm	44.15	48.12	32.13	27.57	62.70	59.70	36.56	62.13
Hardness, IRHD	60.28	65.30	75.28	95.60	92.60	94.68	95.42	99.52
Abrasion resistance, Taber type cm ³ /2000 cyl.	0.0089	0.2062	0.3991	0.4252	0.2895	0.2368	0.4338	0.5370

Figure 4.9a Properties of NR/PVC-P40 and GNR20/PVC-P40 Blends.

Property	Blend NR:PVC-P40				Blend GNR20:PVC-P40			
	90:10	80:20	60:40	40:60	90:10	80:20	60:40	40:60
Tensile strength, MPa	17.40	17.42	7.18	4.72	20.92	20.74	18.15	13.51
E.B., %	827	797	1088	352	680	563	388	227
300% Mod., MPa	2.11	2.69	NA	3.32	6.63	7.62	13.60	NA
Tear strength, N/mm	30.58	32.77	31.32	33.32	35.22	38.12	38.97	32.44
Hardness, IRHD	37.12	41.96	59.30	68.25	45.48	49.28	62.44	74.58
Abrasion resistance, Taber type cm ³ /2000 cyl.	NA	0.6641	0.9325	0.7648	NA	0.0556	0.6117	0.7546

Figure 4.9b Properties of GNR40/PVC-P40 and GNR60/PVC-P40 Blends.

Property	Blend GNR40:PVC-P40				Blend GNR60:PVC-P40			
	90:10	80:20	60:40	40:60	90:10	80:20	60:40	40:60
Tensile strength, MPa	23.79	22.17	18.66	15.73	25.37	21.36	16.95	17.69
E.B., %	537	313	242	168	364	324	222	210
300% Mod., MPa	17.24	20.98	NA	NA	20.00	20.00	NA	NA
Tear strength, N/mm	42.78	45.86	41.98	38.42	63.20	49.05	45.59	51.25
Hardness, IRHD	59.20	63.28	73.52	87.26	91.72	94.70	93.60	97.30
Abrasion resistance, Taber type cm ³ /2000 cycle.	0.0152	0.1278	0.3827	0.4829	0.2405	0.3755	0.5541	0.5523

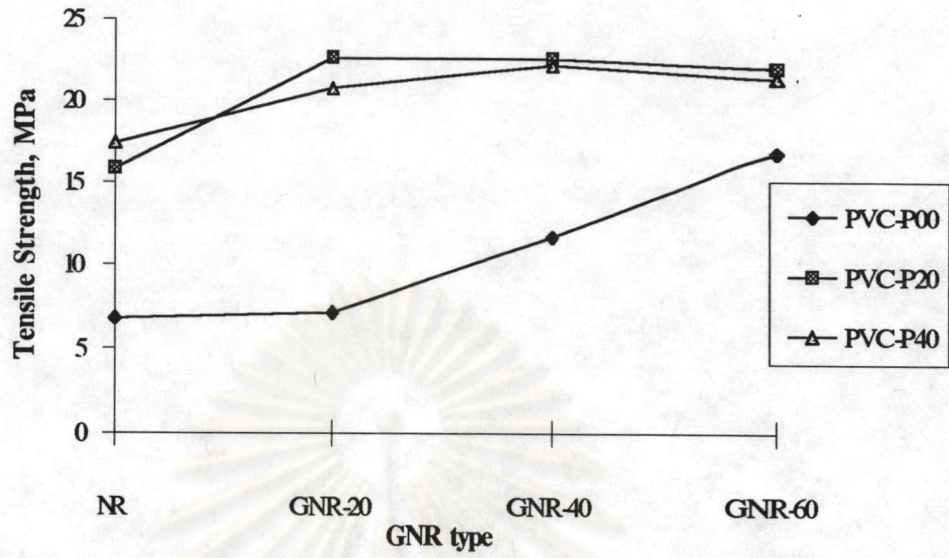


Figure 4.21a Effect of GNR types in GNR/PVC blends (80/20 ratio) on tensile strength.

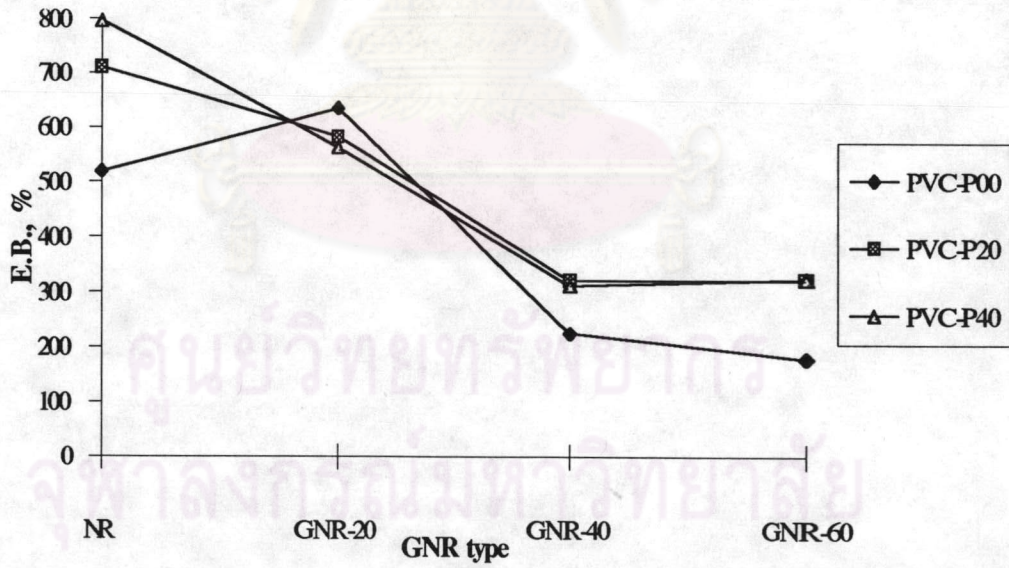


Figure 4.21b Effect of GNR types in GNR/PVC blends (80/20 ratio) on % elongation at break.

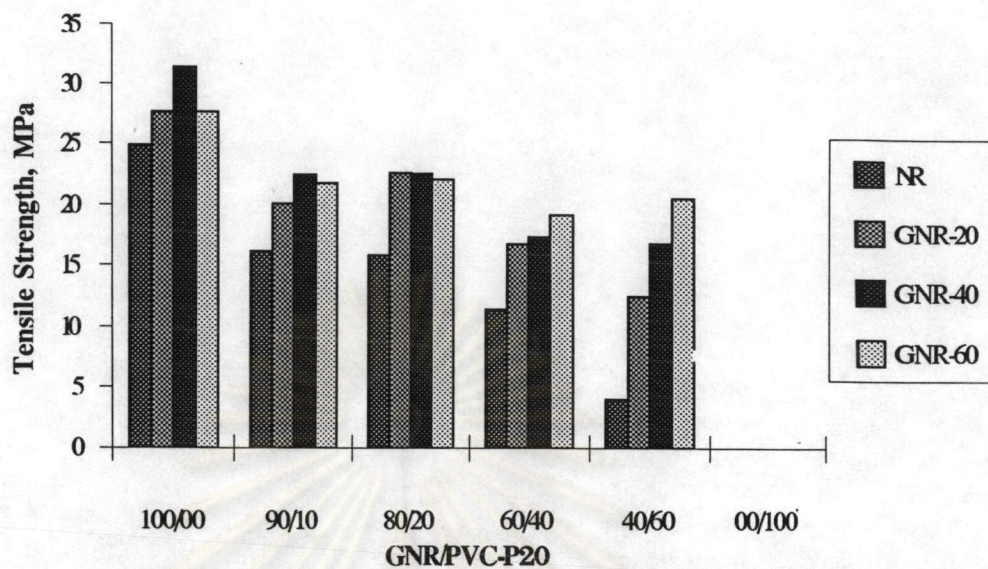


Figure 4.22a Effect of GNR/PVC-P20 ratio on tensile strength.

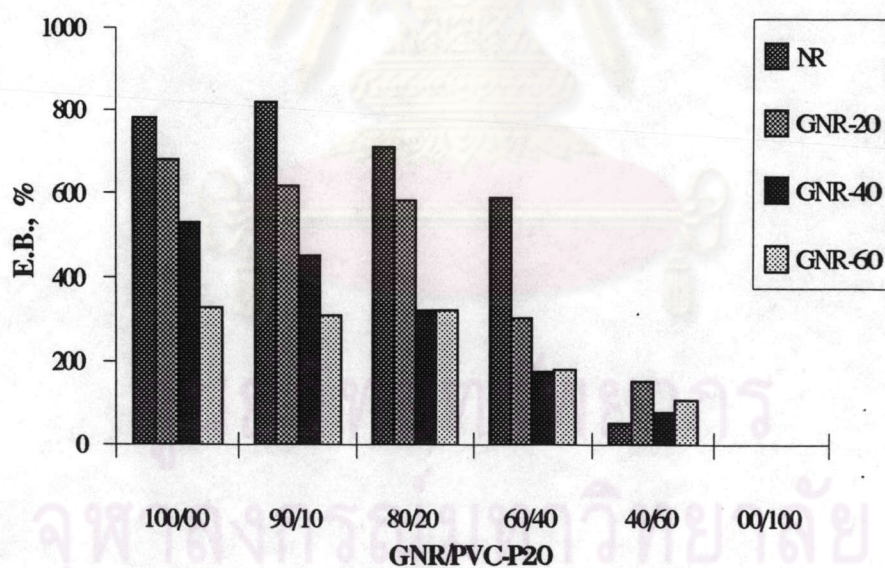


Figure 4.22b Effect of GNR/PVC-P20 ratio on % elongation at break.

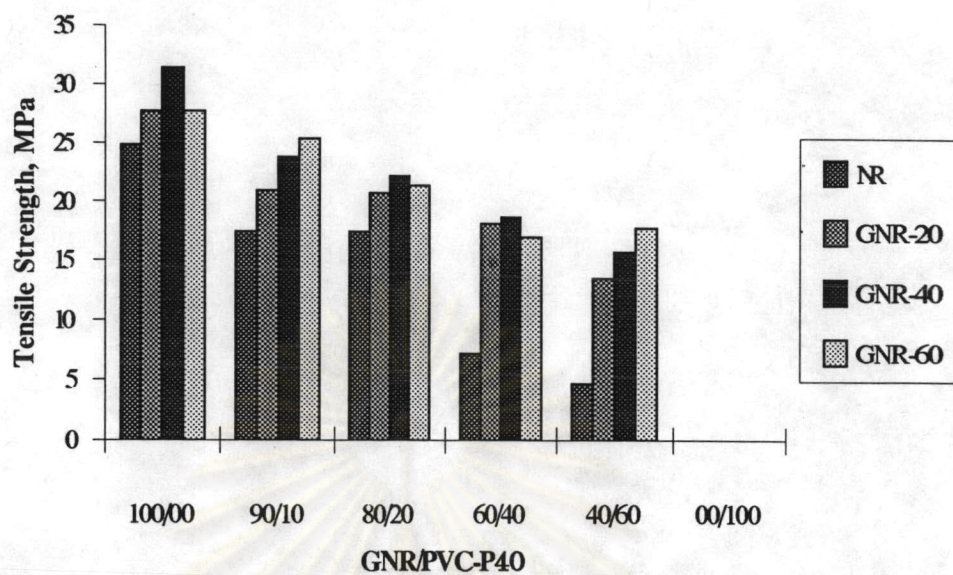


Figure 4.23a Effect of GNR/PVC-P40 ratio on tensile strength.

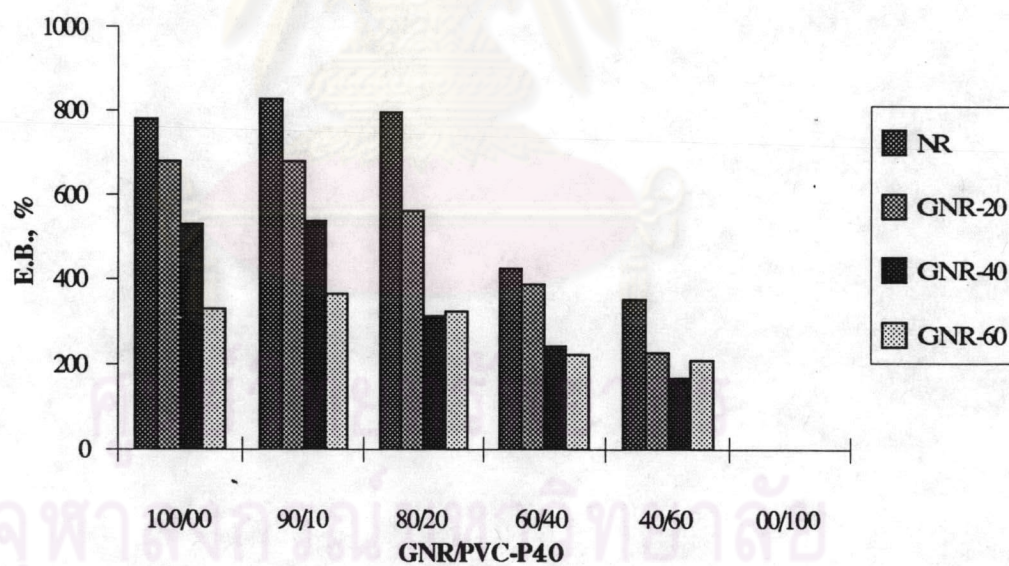


Figure 4.23b Effect of GNR/PVC-P40 ratio on % elongation at break.

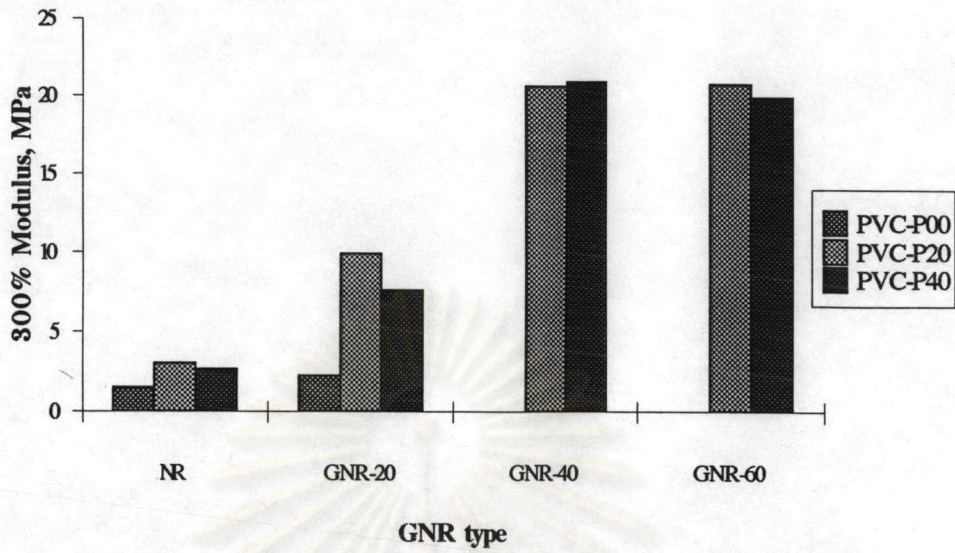


Figure 4.24 Effect of the different GNR in GNR/PVC (80/20) blends on 300% modulus

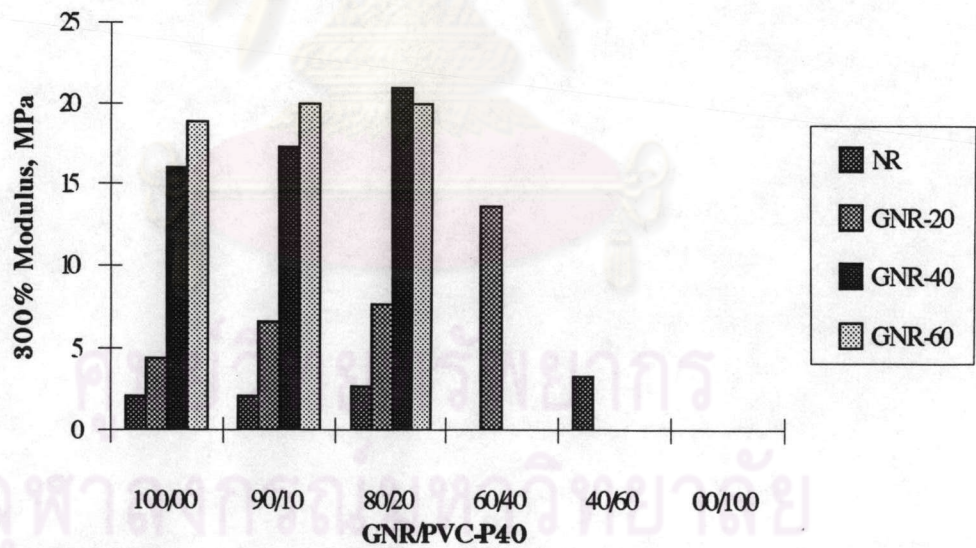


Figure 4.25 Effect of GNR/PVC-P40 ratio on 300% modulus.

4.5.2 Tear strength

The tear strength as a function of MMA content and DOP plasticizer content is shown in Figure 4.26, 4.27 and 4.28. For the GNR/PVC blend compounds, the tear strength considerably increases with a rising amount of MMA. The increase of MMA content may cause the increase of the hard segment of MMA grafted chain and PMMA homopolymer.

From Figure 4.27, 4.28, the tear strength of GNR/PVC blends decreases with increasing plasticized PVC content. The tear strength of the vulcanized blend reached minimum appeared at GNR/PVC ratio of 60:40 and 40:60. At both GNR/PVC ratio, no one component prevailed, both components existed in continuous phases, which would give rise to inferior tear strength. The tear strength increases the following order:

$$\text{GNR-60/PVC} > \text{GNR-40/PVC} > \text{GNR-20/PVC} > \text{NR/PVC}$$

for all GNR/PVC ratios.

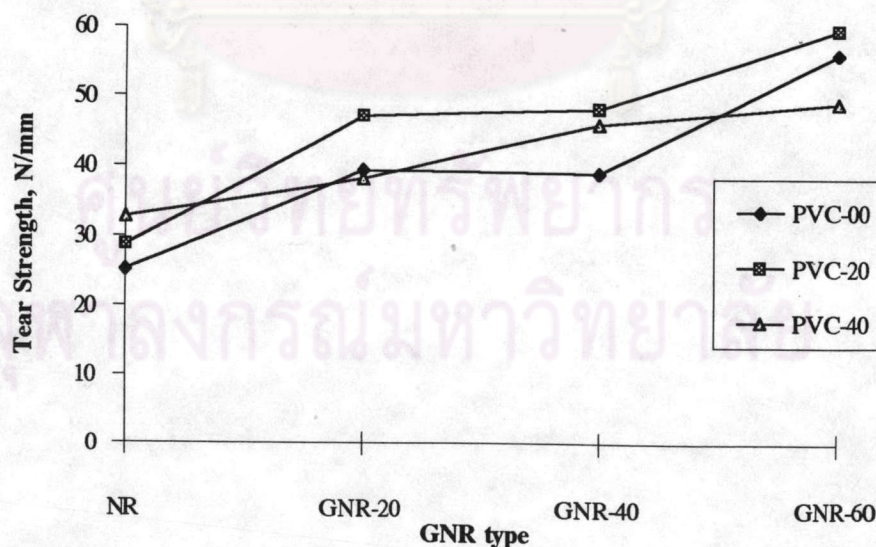


Figure 4.26 Effect of the different GNR types in GNR/PVC blends (80/20 ratio) on tear strength.

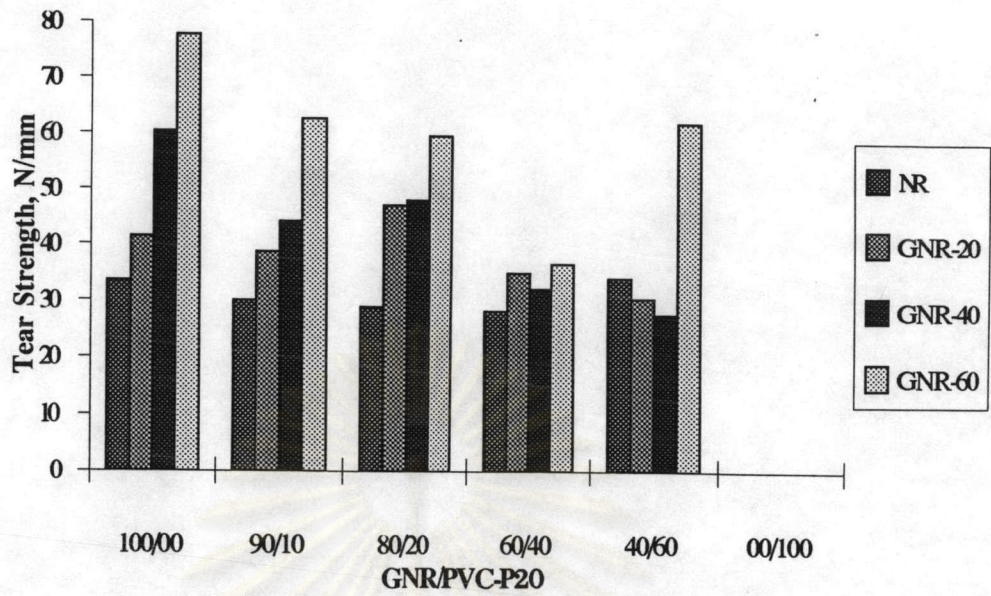


Figure 4.27 Effect of GNR/PVC-P20 ratio on tear strength

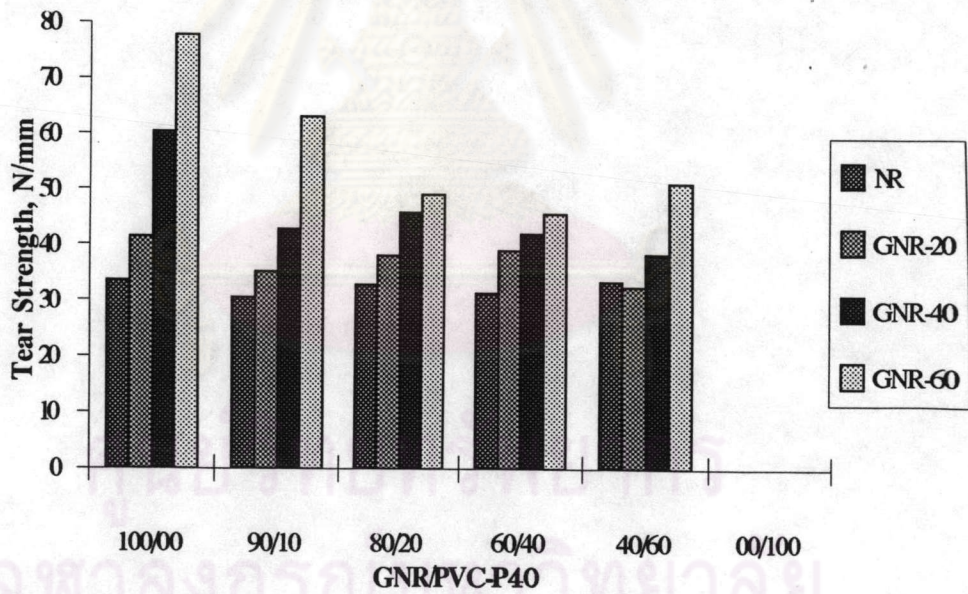


Figure 4.28 Effect of GNR/PVC-P40 ratio on tear strength

4.5.3 Hardness measurement

Hardness of vulcanized GNR/PVC blends are shown in Figure 4.29, 4.30, and 4.31. From Figure 4.29 for GNR/PVC blends, the hardness values increase with increasing MMA content in GNR, due to the increasing MMA content. It can be explained that the PMMA grafted chain may cause the hard segment. In addition, the hardness values of GNR/PVC blends at 80/20 ratio decrease with increasing DOP content in plasticized PVC.

From Figure 4.30 and 4.31, It can be seen that PVC compounds can enhance the hardness property. The hardness increases with increasing PVC component in GNR/PVC blends. The order of hardness follows the sequence:

$$\text{GNR-60} > \text{GNR-40} > \text{GNR-20} > \text{NR.}$$

For the GNR-60/PVC blends, there was a small increase in hardness with increasing the PVC component. The hardness values decreased with increasing amount of rubber. Since vulcanized rubber had more elastic property, consequently the blends deformed easily.

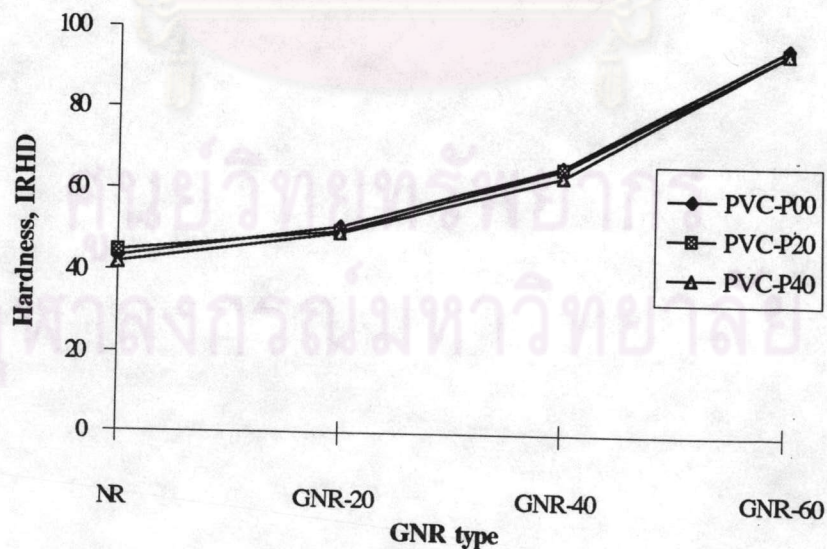


Figure 4.29 Effect of different GNR types in GNR/PVC blends (80/20 ratio) on hardness.

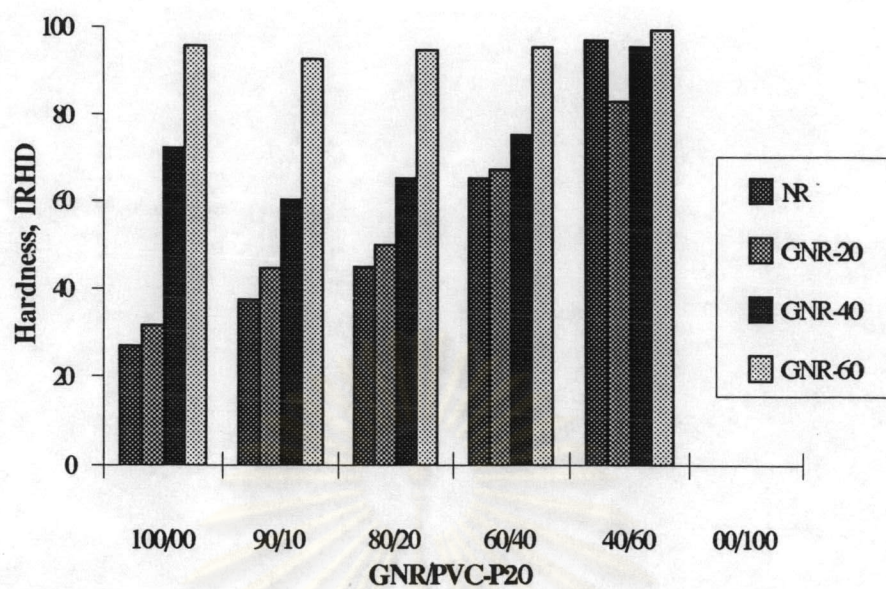


Figure 4.30 Effect of GNR/PVC-P20 blends ratio on hardness.

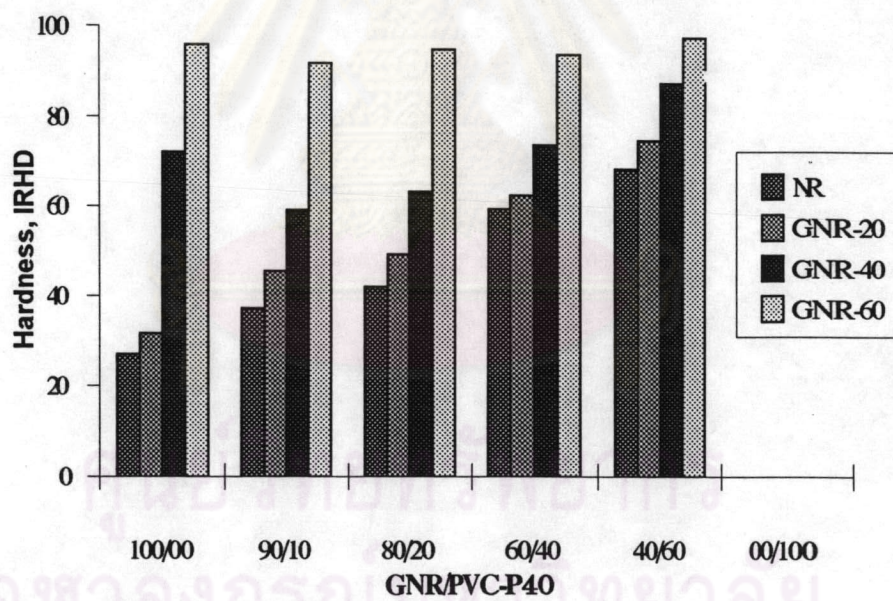


Figure 4.31 Effect of GNR/PVC-P40 blends ratio on hardness.

4.6 Solvent resistance

Swelling of the graft copolymer in toluene/iso-octane mixture was studied. The change in mass (%) from the solvent resistance measurements for different grafted natural rubber compounds are shown in Figure 4.32 and in Appendix D. The solvent resistance of grafted natural rubber was improved due to the graft copolymerization MMA monomer onto NR. The solvent resistance increased (or % swelling decreased) with increasing MMA content because PMMA was polar component in grafted NR (of bulky hydrophobic methyl methacrylate groups in NR backbone), it swelled less in nonpolar solvents and swelled more in polar solvents. For the grafted natural rubber compounds, the solvent resistance can be measured by solvent swelling (%), the lower values of solvent swell, the higher solvent resistance. This result confirms one of the advantages of grafting of MMA onto NR. In addition, the vulcanized rubber compounds also improved the solvent resistance. The reason is that for specific solvent higher the crosslink density of the rubber gives lower the swelling property. Therefore, the oil resistance of NR is improved through the graft copolymerization of MMA onto NR. The oil resistance increases with increasing MMA content.

For GNR/PVC blends, % swelling or solvent resistance are shown in Figure 4.33, 4.34, and 4.35. At higher PVC content, the PVC can enhance the solvent resistance of GNR/PVC blends. This result confirms one of the advantages of the corporation of PVC in GNR/PVC blends. From Figure 4.35, in the blends with the DOP plasticizer above 20 phr, some of DOP plasticizer in blends was extracted by solvent (toluene/iso-octane). It can be observed that the swelling rate decreased slowly. The GNR/PVC blends with the higher DOP plasticizer content, the solvent

resistance decreased with increasing DOP plasticizer content. It can be explained that DOP plasticizer is organic plasticizer which is compatible with organic solvent.

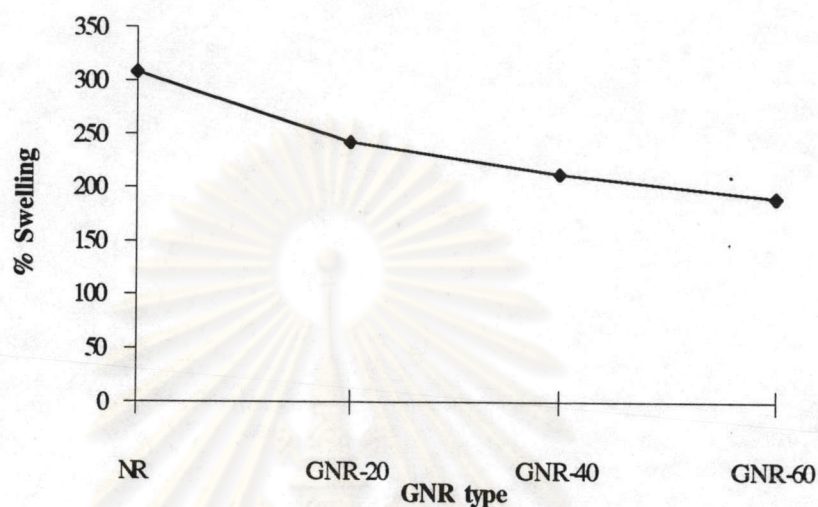


Figure 4.32 Effect of the MMA content (0, 20, 40, 60 phr) in grafted natural rubber on solvent resistance.

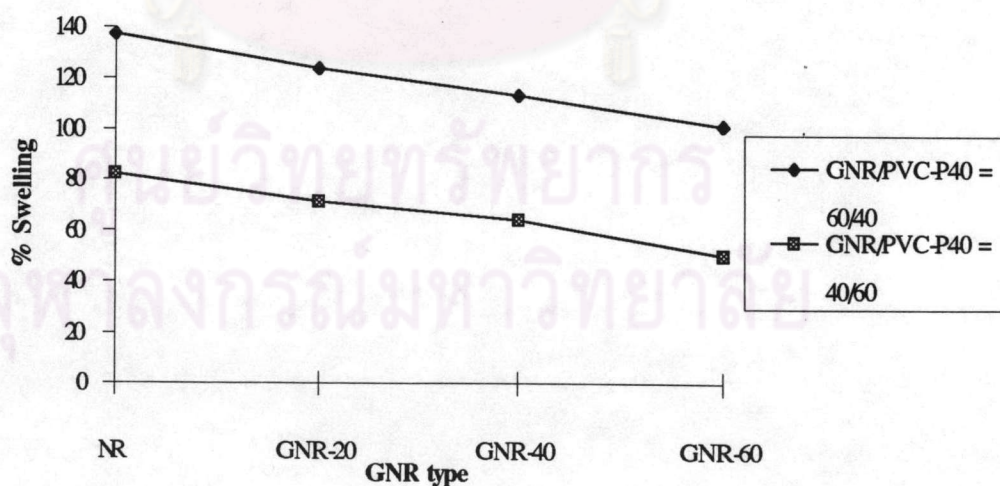


Figure 4.33 Effect of GNR types in GNR/PVC-P40 blends of varying proportions (40/60 and 60/40) on solvent resistance.

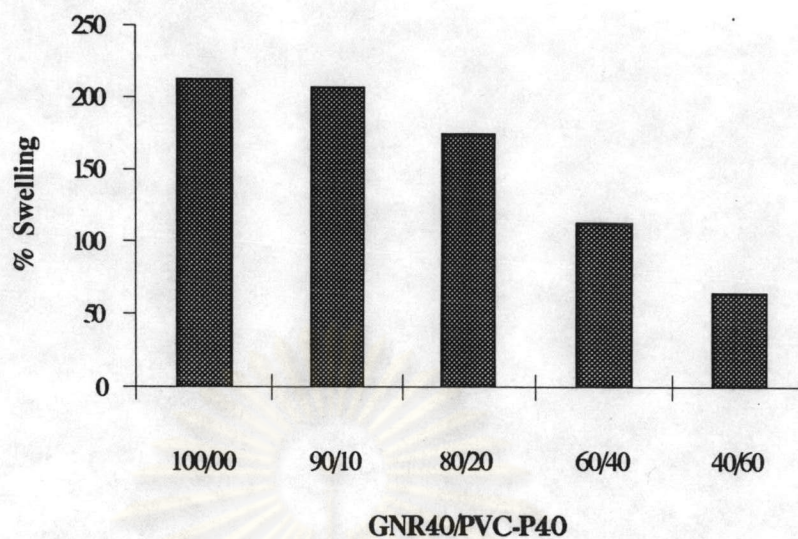


Figure 4.34 Effect of varying proportions of GNR40/PVC-P40) on solvent resistance.

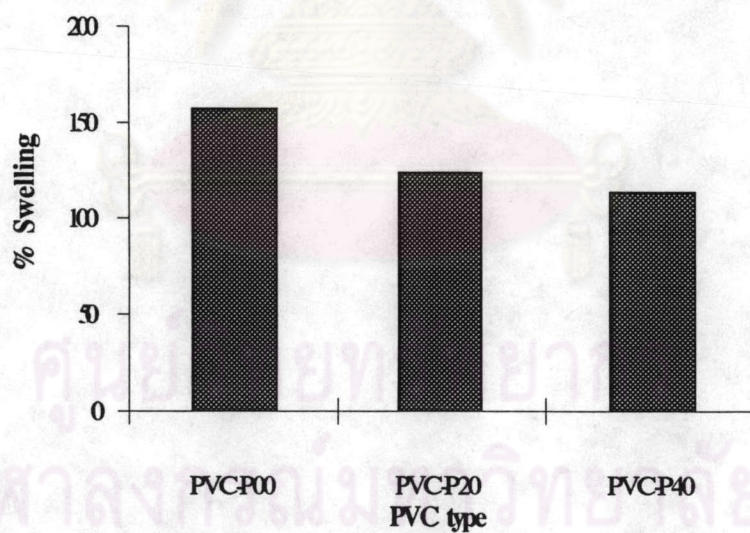


Figure 4.35 Effect of the amount of DOP plasticizer in GNR40/PVC blends (40/60) on solvent resistance.

4.7 Abrasion resistance

The abrasion resistance expressed as the volume loss of natural rubber, grafted natural rubber and GNR/PVC vulcanizates are shown in Figure 4.36, 4.37, and 4.38. For natural rubber and grafted natural rubber vulcanizates, the abrasion resistances was approximately constant as the MMA content increased from 0 to 40 phr, because MMA acted as self-reinforcing in grafted NR vulcanizates. Additional MMA content, above the 40 phr level, the abrasion resistance decreased, it can be explained that PMMA acted similar to the filler to improve hardness.

For GNR/PVC vulcanizates, the abrasion resistance decreased with decreasing the GNR/PVC ratio, because PVC may be immiscible to NR or GNR. For the GNR/PVC vulcanizates, the abrasion resistance had a trend to increase with increasing the MMA content in GNR. For the comparison of NR and different GNR at GNR/PVC ratio (80/20), the rate of abrasion resistance increases in the following order:

$$\text{GNR-40} > \text{GNR-20} > \text{NR.}$$

It can be explained that the MMA in GNR from 20 to 40 phr could improve the patially miscibility of GNR/PVC vulcanizates. The GNR-60/PVC vulcanizates with the PVC content above 40%, the abrasion resistance decreased because GNR-60 vulcanizates containing high MMA could not acts as reinforcement (but acted as filler). Therefore, the GNR-40 was appropriated for mixing with PVC, the blends had highest abrasion resistance.

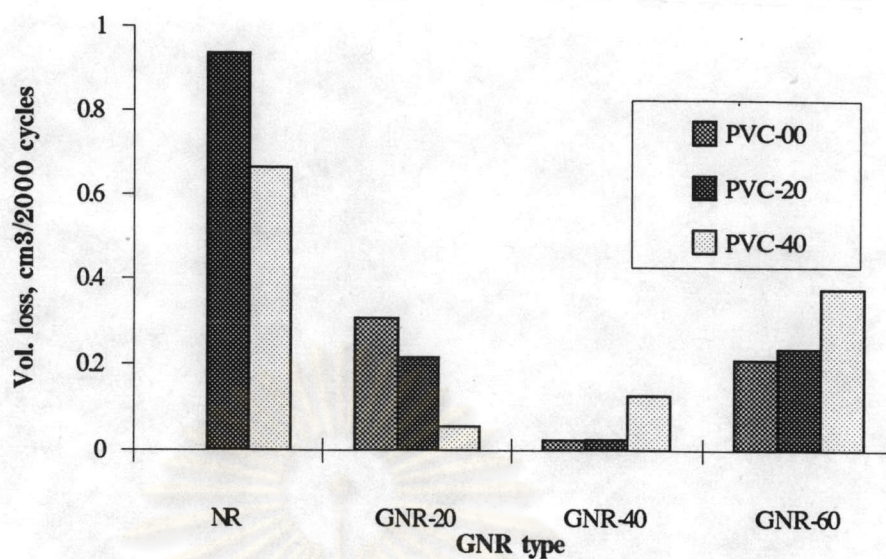


Figure 4.36 Effect of GNR type on abrasion resistance of GNR/PVC blends (80/20 ratio).

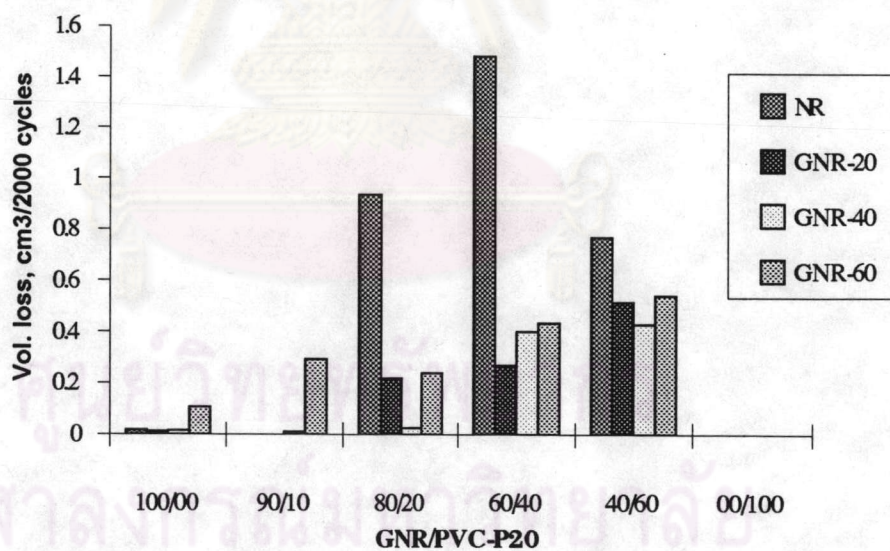


Figure 4.37 Effect of GNR/PVC-P20 ratio on abrasion resistance of GNR/PVC-P20 blends.

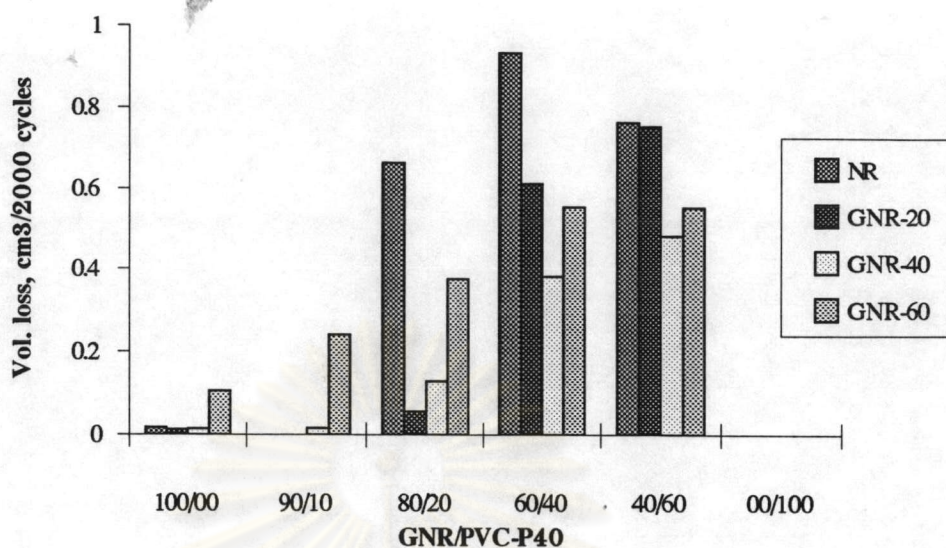


Figure 4.38 Effect of GNR/PVC-P40 ratio on abrasion resistance of GNR/PVC-P40 blends.

4.8 Electron microscopy study

SEM micrographs in Figure 4.39, 4.40, 4.41, and 4.42, the PVC is dispersed in grafted natural rubber matrix. For Figure 4.39 and Figure 4.40, NR/PVC-P20 blend the diameter of PVC-P20 was about 2-3 micron, when the PMMA content in grafted natural rubber (GNR-60/PVC-P20) increased, the particle diameter became smaller and displayed a fine and homogeneous morphology. For improvement the strength of plastics with elastomers, it is well known that the controlled dispersion of the elastomers (grafted natural rubber) in the PVC matrix is one of the most important parameter.

The properties of the both blends (NR/PVC-P20 and GNR-60/PVC-P20) such as tensile strength, tear strength and abrasion resistance are as follows:

	<u>NR/PVC-P20</u>	<u>GNR-60/PVC-P20</u>
Tensile strength, MPa	11.41	19.15
Tear strength, N/mm	28.21	36.56
Hardness, IRHD	65.20	95.42
Abrasion resistance, cm ³ /2000 cycles (Taber abraser type)	1.4811	0.4338

For Figure 4.41 and 4.42, the SEM micrographs of GNR-60/PVC-P00 at ratio of 60:40 and GNR-40/PVC-P40 at ratio of 40:60, the GNR-40/PVC-P40 blend has better homogeneous dispersion than GNR-60/PVC-P00 blend and the properties of this blends were also higher.

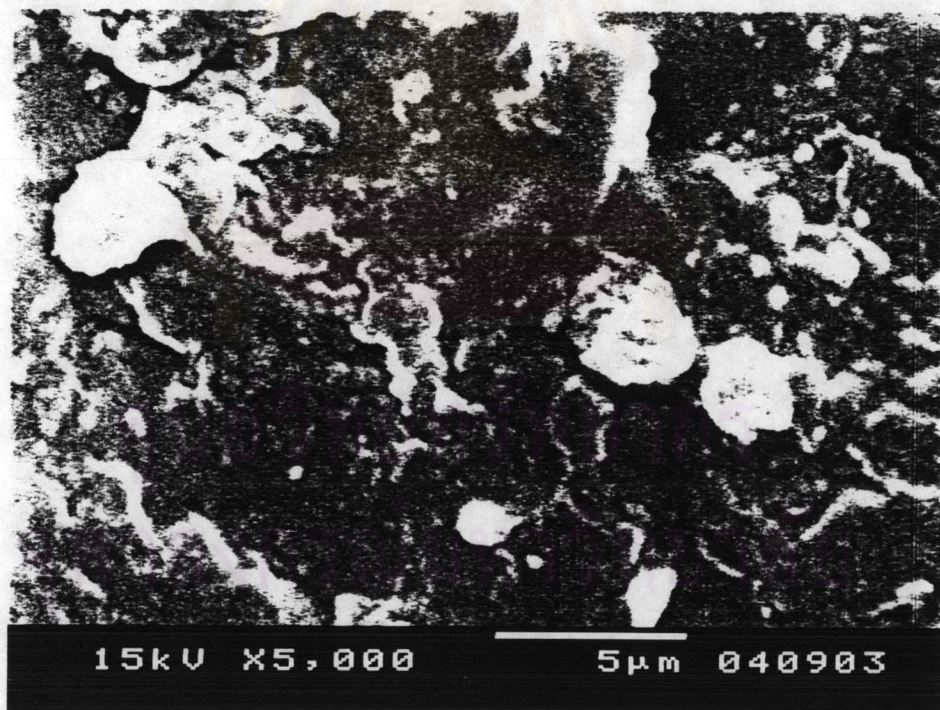


Figure 4.39 SEM photograph of NR/PVC-P20 = 60/40.

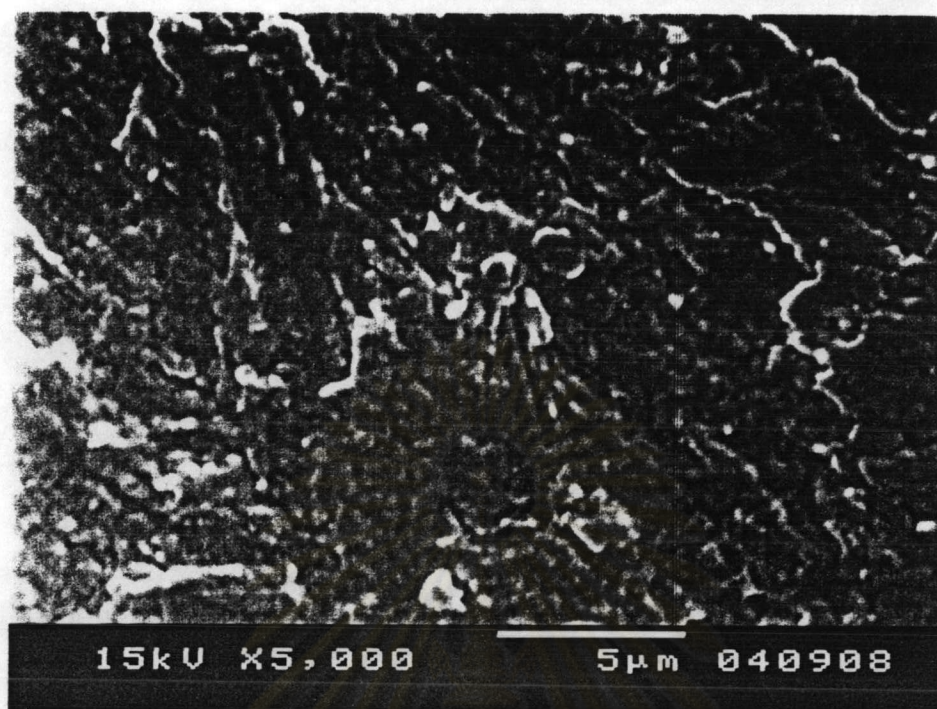


Figure 4.40 SEM photograph of GNR-60/PVC-P20 = 60/40.

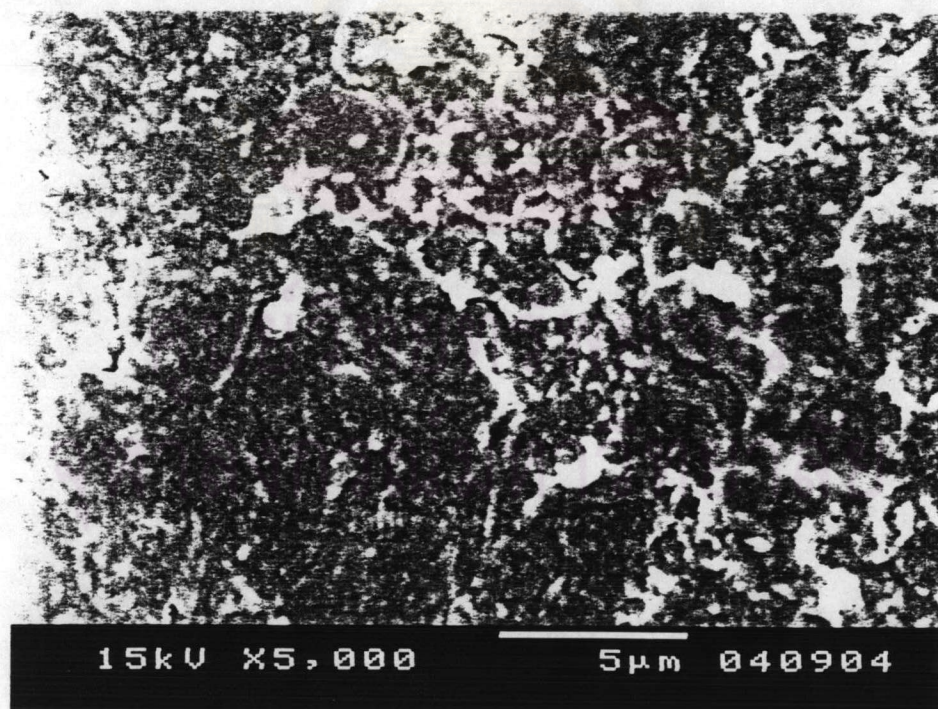


Figure 4.41 SEM photograph of GNR-60/PVC-P00 = 60/40.



Figure 4.42 SEM photograph of GNR-40/PVC-P40 = 40/60.

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