CHAPTER IV

RESULTS AND DISCUSSION

The graft copolymers of glycidyl methycrylate and styrene onto natural rubber were prepared by emulsion polymerization. The redox system of cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) was used to initiate the graft copolymerization. This redox couple consists of an oil-soluble peroxide and a water-soluble amine which could react at the water/particle interface [23, 24]. The effects of initiator concentration, reaction temperature, monomer concentration, and reaction time on the grafting efficiency were investigated. The natural rubber-g-styrene and glycidyl methacrylate was used as a compatibilizer in natural rubber/PMMA blends. The natural rubber, STR5L, was blended with PMMA at various the grafted natural rubber (NR-g-St/GMA) contents as compatibilizer using a two roll-mill and a compression molding. The mechanical properties of the natural rubber/PMMA blends were investigated.

4.1 Properties of Natural Rubber Latex

The natural rubber latex obtained from Thai Rubber Latex (Thailand) Co. Ltd. has the properties as shown in Table 4.1.

Table 4.1 The Properties of High Ammonia Natural Rubber Latex

Properties	Test Results
Total Solid Content, %	61.54
Dry Rubber Content, %	60.03
Non Rubber Solids, %	1.56
Ammonia Content (on Total Weight), %	0.70
Ammonia Content (on Water Phase), %	1.82
pH Value	10.92
KOH Number	0.5610
Volatile Fatty Acid Number (VFA)	0.0194
Mechanical Stability Time@ 55% TS.,Su.	1,100 on 11/07/2001
Specific Gravity at 25°C	0.9411
CST.(ml.)	2.4
Magnesium Content (ppm)	23
Viscosity (60% TS. Spindle no. 1.60 rpm.) cps.	64
Remark : Add ammonia laurate 15%-0.048%	
Remark : Free from pentachlorophenol	

4.2 Preparation of Grafted Natural Rubber

The grafted natural rubber was prepared by emulsion graft copolymerization process. The water-insoluble cumene hydroperoxide (CHPO) and water-soluble tetraethylene pentamine (TEPA) were used to initiate the graft copolymerization. The appropriate conditions which yielded high conversion, percentage grafted natural rubber and grafting efficiency were investigated. The mechanism of graft copolymerization was also proposed.

4.2.1 Effect of Initiator Concentration

The graft copolymerization of glycidyl methacrylate and styrene onto natural rubber have been accomplished using the redox initiators, couple cumene hydroperoxide (CHPO)/tetraethylene pentamine. The effects of initiator concentration at various temperatures on the conversion, percentage grafted natural rubber and grafting efficiency are shown in Table 4.2 and Figures 4.1-4.3. The detail of all data and calculation are shown in Appendix A. The parameters of graft copolymerization are as follows:

- amount of styrene and glycidyl methacrylate (70:30) : 100 parts by weight
- rubber content : 100 parts by weight
- emulsifier concentration : 1.5 parts by weight
- initiator concentration : 0.5-5 parts by weight
- reaction temperature : 50-70°C
- reaction time : 10 hours

From Figures 4.1 and 4.2, the conversion and grafting efficiency increase with increasing initiator concentration at various temperature investigated. The increase in initiator concentration produces more grafting sites for styrene/glycidyl methacrylate random copolymers or styrene, glycidyl methacrylate to graft. Therefore, the conversion and grafting efficiency increase. At the higher initiator concentrations, initiator radical is produced more and causes the increase in radical chains to graft but the recombination of two radical chains can occur. So grafting efficiency slightly decrease at high initiator concentration. From Table 4.2, the percentage grafted natural rubber, the conversion and grafting efficiency increase with increasing initiator concentration upto 2.5 phr at all temperature and the percentage grafted natural rubber, the conversion and grafting efficiency did not change so much at initiator concentration above 2.5 phr. From Figure 4.3, it was also found that percentage grafted natural rubber increases, percentage free natural rubber decreases and percentage free St/GMA

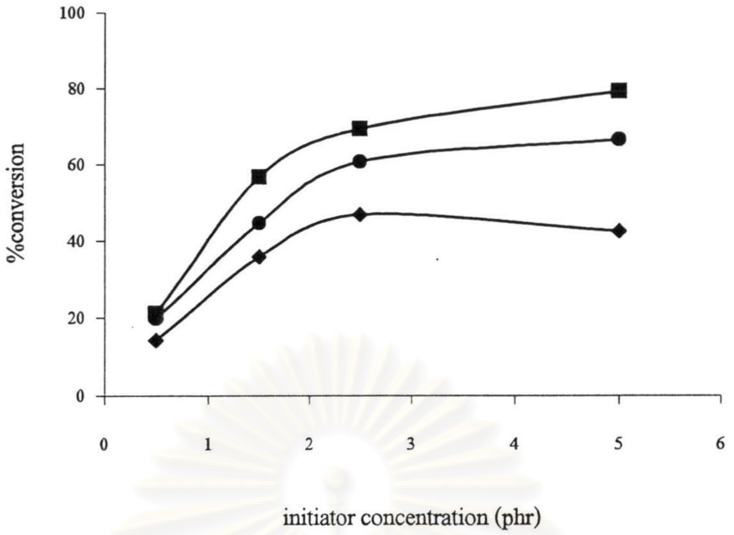


Figure 4.1 Effect of the Initiator Concentration on the Conversion (Monomer 100 phr, 50-70°C , 10 h) : (◆) 50°C; (■) 60°C; and (●) 70°C

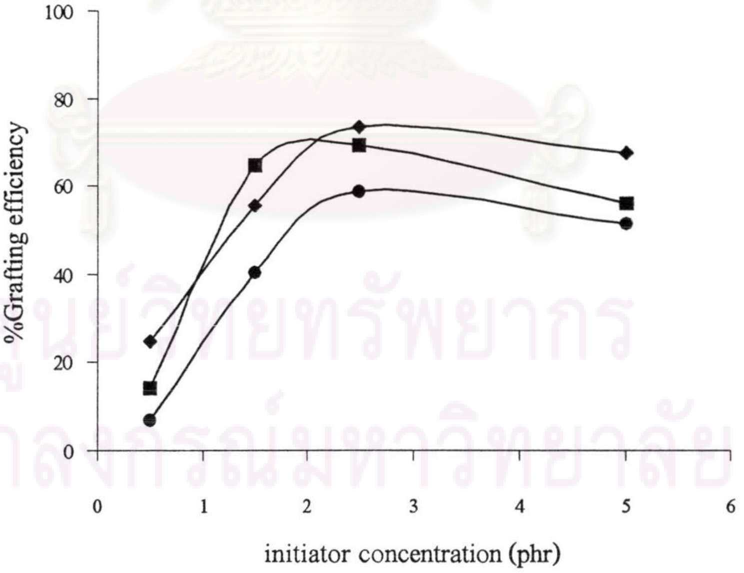


Figure 4.2 Effect of the Initiator Concentration on the Grafting Efficiency (Monomer 100 phr, 50-70°C, 10 h) : (◆)50°C; (■) 60°C; and (●) 70°C

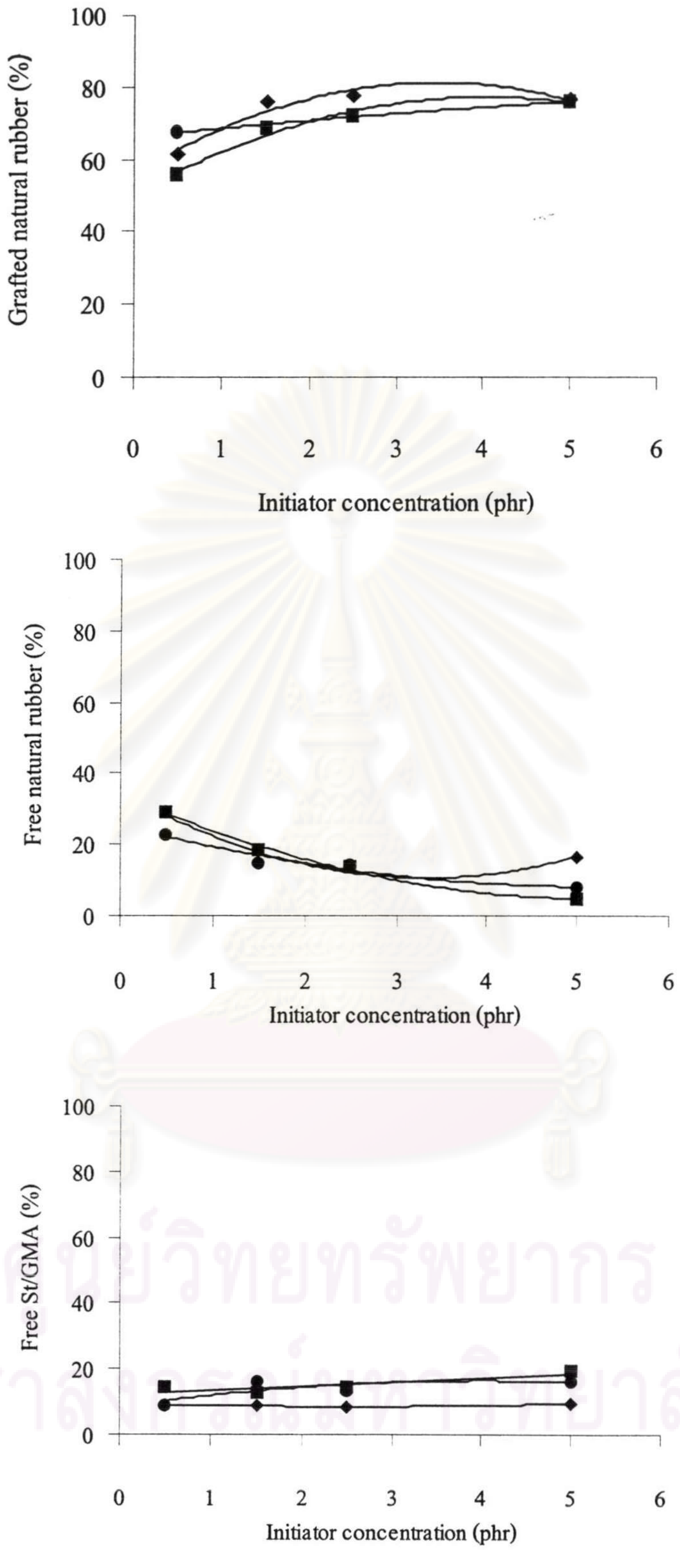


Figure 4.3 Effect of the Initiator Concentration on the Percentage Grafted Natural Rubber, Percentage Free Natural Rubber, and Percentage Free St/GMA (Monomer 100 phr, 50-70°C, 10 h) : (◆) 50°C; (■) 60°C; and (●) 70°C

Table 4.2 Effect of Initiator Concentration on the Conversion, Grafting efficiency, and Percentage Grafted Natural Rubber (T = 50-70°C, Monomer = 100 phr, and Time = 10 h)

	50°C				60°C				65°C				70°C			
Initiator concentration, phr	0.5	1.5	2.5	5	0.5	1.5	2.5	5	0.5	1.5	2.5	5	0.5	1.5	2.5	5
Conversion (%)	14.1	35.7	46.8	42.3	21.1	56.7	69.3	79.1	19.9	44.6	60.6	66.5	11.1	37.3	47.9	50.9
Grafting efficiency (%)	24.8	55.4	73.2	67.4	14.2	64.7	69.3	56.1	23.7	40.9	60.6	69.3	6.9	40.2	58.6	51.5
Grafted natural rubber (%)	61.6	75.9	77.4	76.4	55.8	68.8	71.8	75.8	51.4	66.2	73.3	77.1	67.7	68.9	72.2	75.7
Free natural rubber (%)	29.2	15.0	14.0	16.5	29.2	18.3	13.5	4.7	35.9	16.4	11.7	10.6	23.0	14.7	14.3	7.9
Free St/GMA (%)	9.1	9.0	8.4	9.6	14.8	12.7	14.6	19.4	12.6	17.3	14.8	12.1	9.2	16.2	13.3	16.3

slightly increases with increasing initiator concentration at all temperature investigated. It can be explained that the resulting macroradicals initiate chain growth reactions leading to the production of graft copolymers and homopolymers. The appropriate initiator concentration which give high conversion and grafting efficiency was found to be 2.5 parts by weight at temperature range of 50-70°C.

4.2.2 Effect of Reaction Temperature

The effect of reaction temperature on percentage grafted natural rubber, the conversion and grafting efficiency are shown in Table 4.3 and Figure 4.4. The detail of all data and calculation are shown in Appendix A. The parameters of graft copolymerization are as follows:

- amount of styrene and glycidyl methacrylate (70:30) : 100 parts by weight
- rubber content : 100 parts by weight
- emulsifier concentration : 1.5 parts by weight
- initiator concentration : 2.5 parts by weight
- reaction temperature : 50-70°C
- reaction time : 10 hours

From Figures 4.4a and 4.4b, the higher temperature results in the decrease of the conversion, grafting efficiency and percentage grafted natural rubber. It is known that the rate of decomposition of initiator depends on the reaction temperature. The cumene hydroperoxide has half life temperature of 158°C/10 h, 180°C/1 h and 250°C /1 min [25]. In this study, tetraethylene pentamine was used to promote cumene hydroperoxide which was decomposed rapidly at a low temperature [23, 24]. As reaction temperature increase, more cumene hydroperoxyl radicals were produced and transferred to the rubber chain then polymerize to form the graft copolymers. The conversion and grafting efficiency increase with increasing polymerization temperature up to 60°C, and then both the conversion and grafting efficiency decrease. This is due to the rapid decomposition of the initiator yielding a high instantaneous radical concentration and the radicals might be acting as radical scavengers. The radicals underwent either recombination, or other side reaction, the initiator efficiency is thus reduced. Therefore, the appropriate reaction temperature which give high conversion and grafting efficiency was 60°C.

Table 4.3 Effect of Reaction Temperature on the Conversion, Grafting Efficiency, and Percentage Grafted Natural Rubber (Initiator Concentration = 2.5 phr, Monomer = 100 phr, and Time = 10 h)

	Reaction Temperature (°C)			
	50	60	65	70
Conversion (%)	46.8	69.3	60.6	47.9
Grafting efficiency (%)	73.2	39.3	60.6	58.6
Grafted natural rubber (%)	77.4	71.8	73.3	72.2
Free natural rubber (%)	14.0	13.5	11.7	14.3
Free St/GMA (%)	8.4	14.6	14.8	13.3

4.2.3 Effect of Monomer Concentration

The effect of monomer concentration on the conversion, percentage grafted natural rubber, and grafting efficiency were investigated. The detail of all data and calculation are shown in Appendix A. The parameters of graft copolymerization are as follows :

- amount of styrene and glycidyl methacrylate (70:30) : 50-150 parts by weight
- rubber content : 100 parts by weight
- emulsifier concentration : 1.5 parts by weight
- initiator concentration : 2.5 parts by weight
- reaction temperature : 60°C

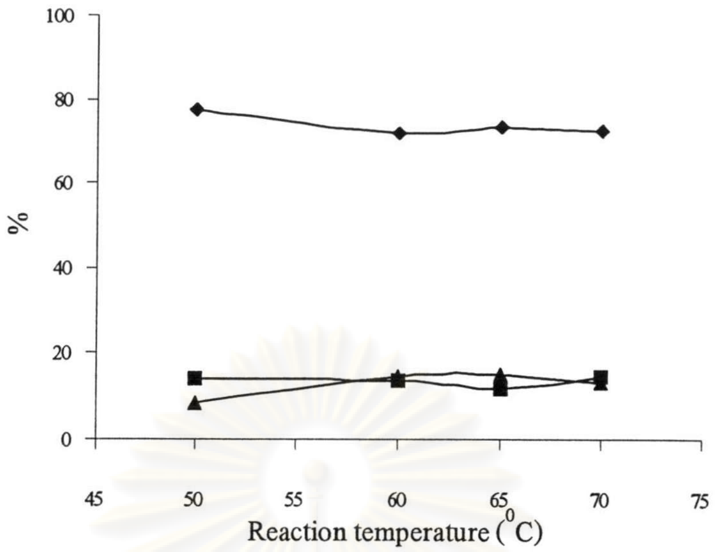


Figure 4.4a Effect of Reaction Temperature on Percentage Grafted Natural Rubber (◆), Percentage Free Natural Rubber (■), Percentage Free St/GMA (▲) : T = 50-70°C, Monomer = 100 phr and Time = 10 h

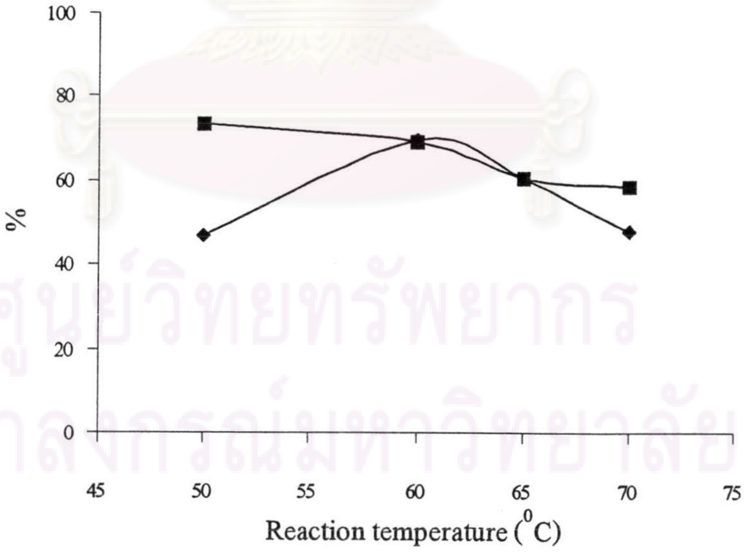


Figure 4.4b Effect of Reaction Temperature on the Conversion (◆) and Grafting Efficiency (■) : T = 50-70°C, Monomer = 100 phr and Time = 10 h

- reaction time : 10 hours

Natural rubber latex particles were swollen with monomer, styrene and glycidyl methacrylate, which was then polymerize using the redox initiator, couple cumene hydroperoxide/tetraethylene pentamine. Most of the free radicals are produced at the monomer swollen particle/water interface [26]. From Table 4.4, as the monomer concentration increases, the conversion and grafting efficiency increase and then slightly decrease. From Figures 4.5a and 4.5b, percentage grafted natural rubber, grafting efficiency and the conversion reach maximum at monomer concentration of 100 phr, and thereafter decrease. In addition, during the grafting of monomer radicals, styryl radicals and GMA radicals, continuously transfers onto natural rubber macroradicals and the ability of natural rubber macroradical to initiate grafting reaction would depend upon the availability of the monomer molecules in their vicinity [11]. The newly arriving monomers are sterically hindered, this results may be limiting the grafting reaction at high monomer concentrations.

Table 4.4 Effect of Monomer Concentration on the Conversion, Grafting Efficiency, and Percentage Grafted Natural Rubber (Initiator Concentration = 2.5 phr, T = 60°C, and Time = 10 h)

	Monomer Concentration, phr				
	50	75	100	125	150
Conversion (%)	35.7	38.2	65.5	58.6	57.4
Grafting efficiency (%)	26.3	41.1	67.2	63.8	59.9
Grafted natural rubber (%)	73.5	68.9	71.7	66.7	46.0
Free natural rubber (%)	14.6	18.1	15.7	17.6	34.9
Free St/GMA (%)	11.8	12.9	12.5	15.6	19.0

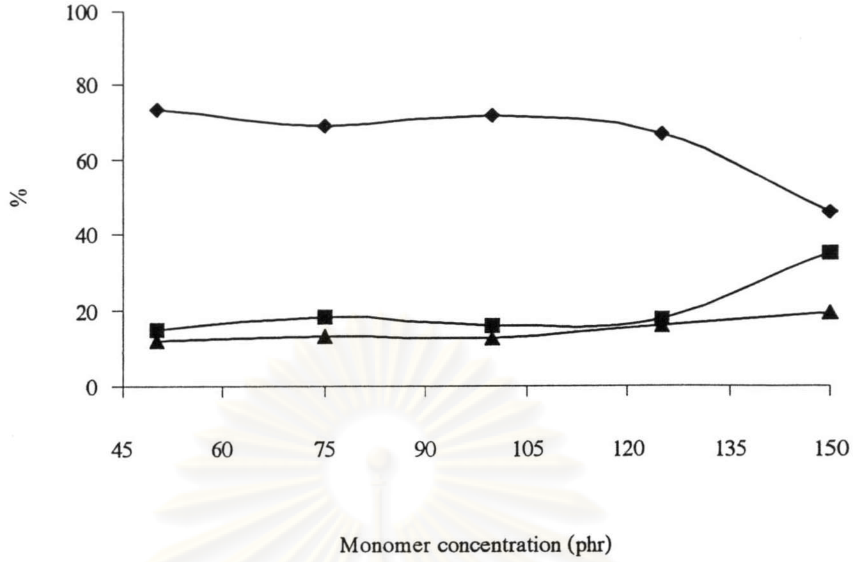


Figure 4.5a Effect of Monomer Concentration on Percentage Grafted Natural Rubber (◆), Percentage Free Natural Rubber (■), Percentage Free St/GMA (▲) : T = 60°C, Monomer = 50-150 phr and Time = 10 h

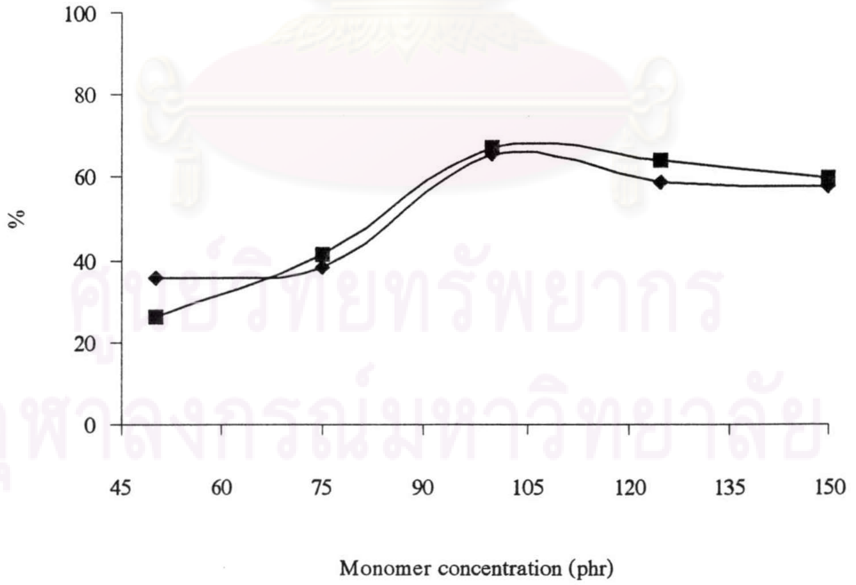


Figure 4.5b Effect of Monomer Concentration on the Conversion (◆) and Grafting Efficiency (■) : T = 60°C, Monomer = 50-150 phr and Time = 10 h

4.2.4 Effect of Reaction Time

The effect of reaction time on the grafting of styrene and glycidyl methacrylate onto natural rubber are shown in Table 4.5 and Figures 4.6a and 4.6b. The detail of all data and the calculation are shown in Appendix A. The parameters of graft copolymerization are as follows :

- amount of styrene and glycidyl methacrylate (70:30) : 100 parts by weight
- rubber content : 100 parts by weight
- emulsifier concentration : 1.5 parts by weight
- initiator concentration : 2.5 parts by weight
- reaction temperature : 60°C
- reaction time : 4-10 hours

Table 4.5 Effect of Reaction Time on the Conversion, Grafting Efficiency, and Percentage Grafted Natural Rubber (Initiator Concentration = 2.5 phr, Monomer = 100 phr, and T = 60°C)

	Reaction Time, h		
	4	8	10
Conversion (%)	17.9	63.3	65.5
Grafting efficiency (%)	3.1	60.9	67.2
Grafted natural rubber (%)	59.5	66.7	71.7
Free natural rubber (%)	25.9	18.0	15.7
Free St/GMA (%)	14.4	15.2	12.5

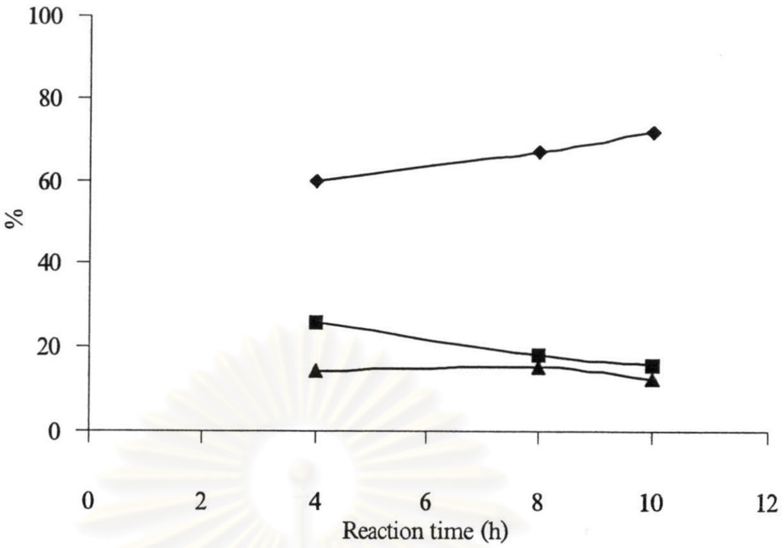


Figure 4.6a Effect of Reaction Time on Percentage Grafted Natural Rubber (◆), Percentage Free Natural Rubber (■), Percentage Free St/GMA (▲) : T = 60°C , Monomer = 100 phr and Time = 4-10 h

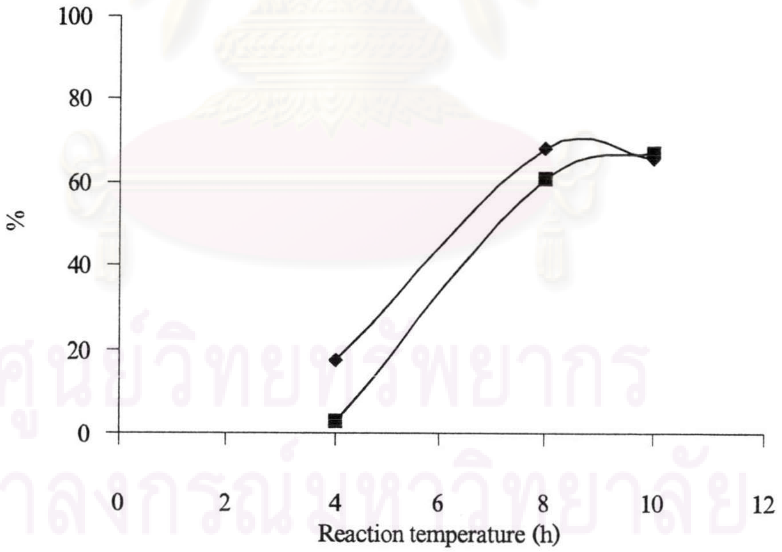


Figure 4.6b Effect of Reaction Time on the Conversion (◆) and Grafting Efficiency (■) : T = 60°C, Monomer = 100 phr and Time = 4-10 h

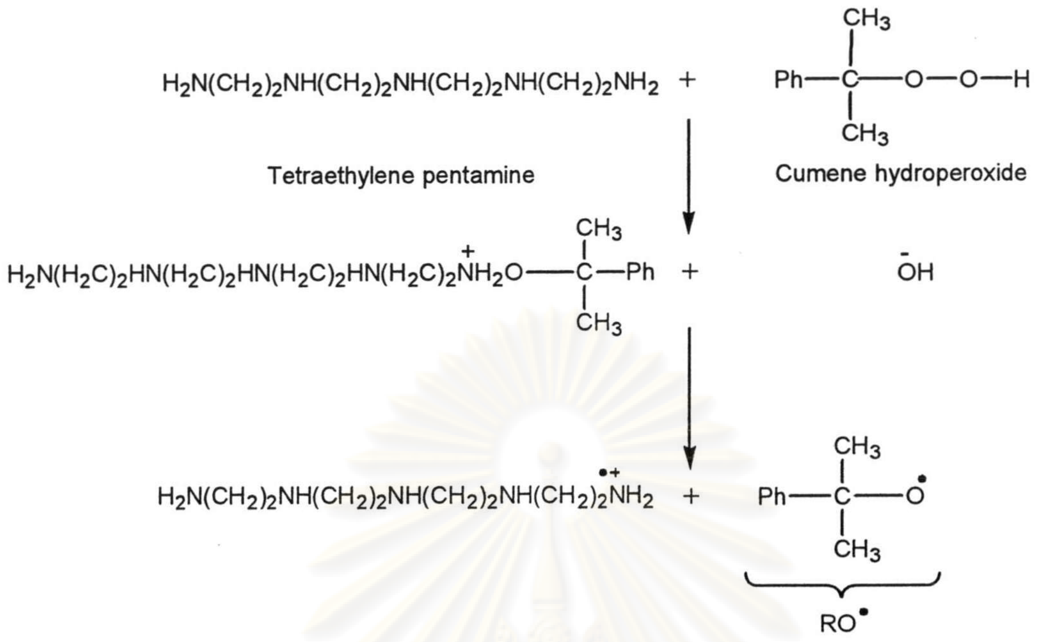
From Figure 4.6b, the conversion and grafting efficiency increases with increasing reaction temperature. The conversion at reaction time of 8 and 10 hours are not different but grafting efficiency at the reaction time of 10 hours is higher than that at the reaction time of 8 hours. Increase in reaction time give the probability of monomer radicals to produce the graft copolymers. It can be seen from Figure 4.6a that percentage grafted natural rubber increase with reaction time and it was also confirmed by the observation of grafted natural rubber morphology using transmission electron microscopy (section 4.4).

Optimum condition for preparation of the grafted natural rubber was found as follows : the rubber content of 100 phr, the initiator concentration of 2.5 phr, the monomer concentration (St/GMA = 70:30) of 100 phr, the reaction temperature of 60 °C, and the reaction time of 10 hours which gave the conversion of 69.3, grafting efficiency of 69.3, and percentage grafted natural rubber of 71.8.

4.3 Mechanism of Free Radical Grafting of Styrene and Glycidyl Methacrylate onto Natural Rubber

a) Initiation

The addition of promoter, tetraethylene pentamine (TEPA) to cumene hydroperoxide causes the latter to decompose rapidly. The decomposition involves the formation of an unstable ionic intermediate (Equation 4.1) that reacts further to give cumene hydroperoxyl radical and a radical cation (Equation 4.2) [9].

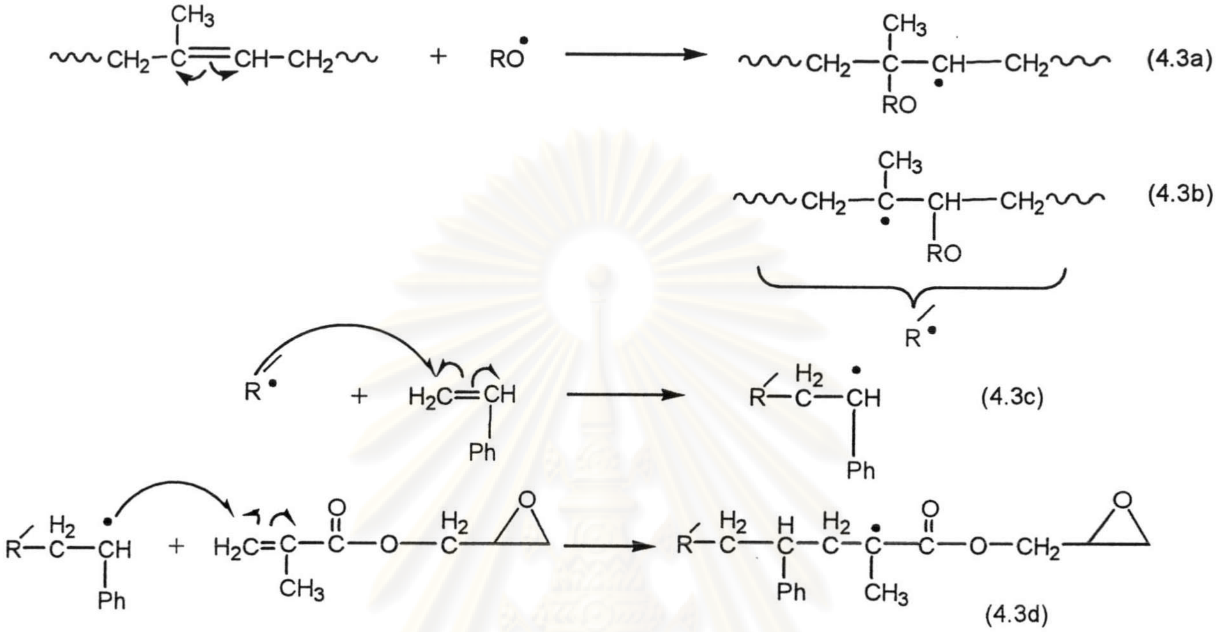

(4.1)

(4.2)

b) Propagation

i) Free Radical Grafting of Styrene and Glycidyl Methacrylate onto Natural Rubber

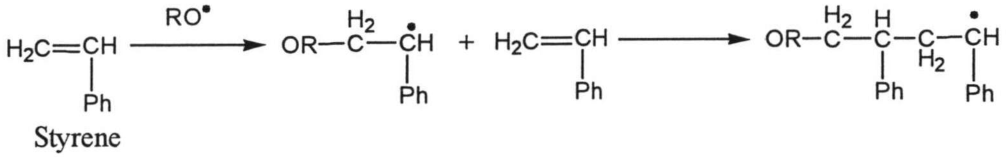
The reactivity of a macroradical toward a vinyl monomer is usually low. A macroradical of a hydrocarbon polymer backbone is nucleophilic and prefers to react with an electropositive double bond and the accessibility of a macroradical is reduced by the bulkiness of the macromolecular chain. For GMA, both electronic and steric effects do not favour its free radical grafting reactivity. The best way to favour the grafting is the addition of a second monomer (styrene) which has a high reactivity toward the macroradicals and the resulting macroradicals are capable of reacting (or copolymerizing) with GMA monomer [12]. It is proposed that cumene hydroperoxyl radicals attach to the backbone unsaturation in natural rubber though carbon-to-carbon bonds to give secondary macroradical (Equation 4.3a) and tertiary macroradical (Equation 4.3b). For the comparison of the reactivity ratio between styrene and glycidyl methacrylate, (r_{GMA} = 0.55 and r_{St} = 0.45), the styryl radicals have a high reactivity toward the macroradicals than GMA radicals [27]. Styrene reacts first with natural rubber macroradicals and the resulting styryl radicals (Equation 4.3c) then copolymerize readily with GMA [12].



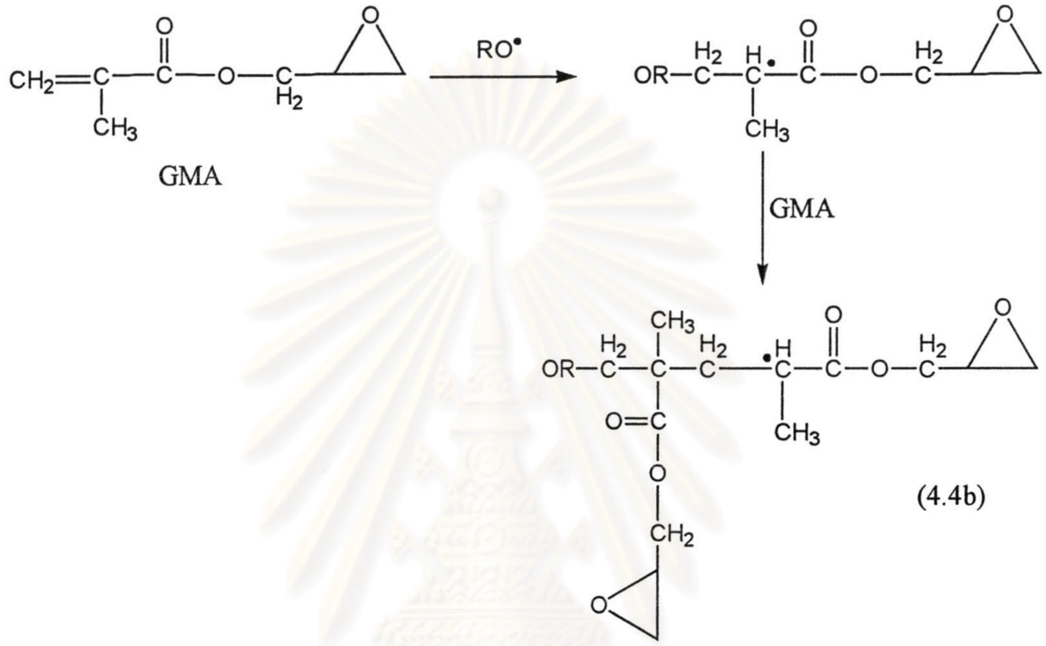
In emulsion polymerization, epoxy group of glycidyl methacrylate could be break by water and potassium hydroxide (Equation 4.3e) and the results are confirmed by FT-IR and NMR spectroscopy.

ii) Polymerization of the Monomer Itself

Polymerization of monomer itself, both styrene and glycidyl methacrylate can be occurred. It is proposed that the cumene hydroperoxyl radical initiate double bond of the monomer to give the radical (styryl radical (Equation 4.4a) or GMA radical (Equation 4.4b)) which then react with other styrene or glycidyl methacrylate monomers.



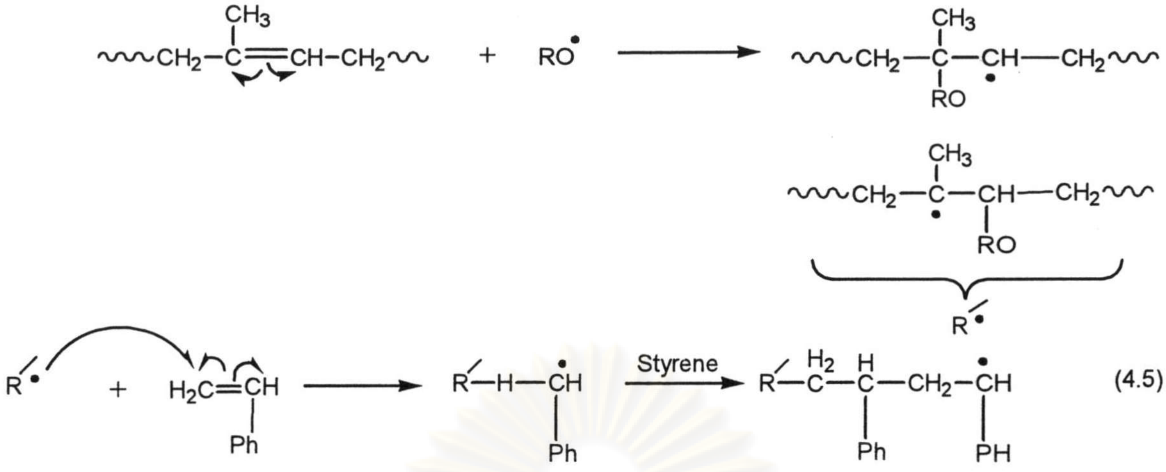
(4.4a)



(4.4b)

iii) Free Radical Grafting of Styrene onto Natural Rubber

Cumene hydroperoxyl radical initiates the double bond of natural rubber to give secondary and/or tertiary natural rubber macroradicals. Then, styrene reacts with the natural rubber macroradicals and the resulting styryl radical then copolymerize with other styrene monomer (Equation 4.5).

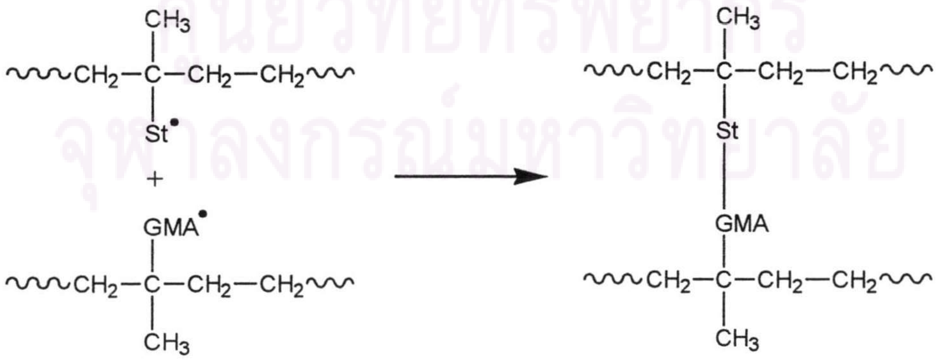


(4.5)

c) Termination

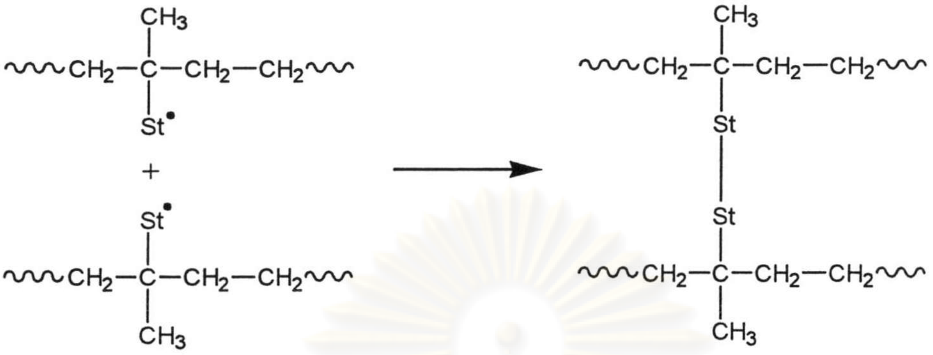
The macroradicals may be terminated by two competing pathways. They can either initiate the grafting of the monomer (which is desirable) or branching/ or crosslinking [12]. In this work, the grafted natural rubber was not all soluble in $CHCl_3$ or toluene and gel formation was found. Therefore, the crosslinking could be occurred by recombination of two macroradicals.

i) Recombination between Styryl and GMA Macroradicals



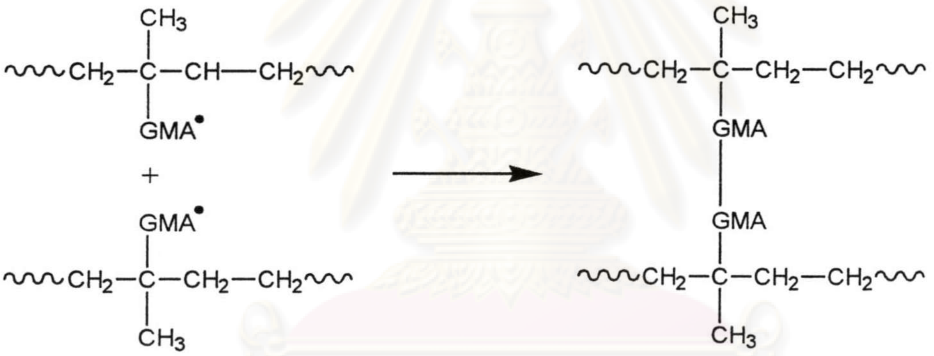
(4.6)

ii) Recombination between Styryl Macroradicals



(4.7)

iii) Recombination between GMA Macroradicals



(4.8)

4.4 Grafted Natural Rubber Morphology

Graft copolymerization is a surface-controlled process because the bipolar redox initiator couple cumene hydroperoxide/tetraethylene pentamine favours the particle/water interface as the locus of polymerization [23]. The grafting of styrene and glycidyl methacrylate onto natural rubber is a core-shell type, emulsion polymerization. The grafted natural rubber particles consist of the natural rubber core and the compatibilized St/GMA shell. During the course of polymerization, old polymer molecules would be encapsulated with new polymer molecules and gave the pathway (Figure 4.7) to the postulated encapsulation mechanism [28].

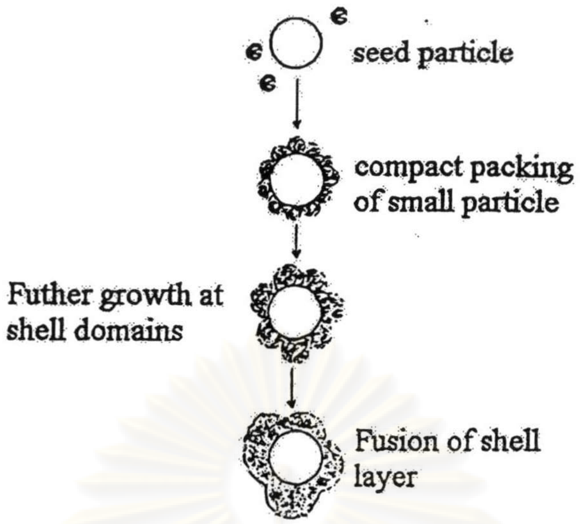


Figure 4.7 Pathway to Prepare Core/Shell Particle [28]

From Figure 4.8 shows TEM micrographs of grafted natural rubber latex particles by styrene and glycidyl methacrylate (70:30) of 100 phr. The darker areas represent the natural rubber core regions, while the lighter areas are St/GMA film as shell. The presence of nodules on the surface of the graft copolymers may be due to the growing macroradical chains, which are grafted onto the surface of natural rubber particle and continue to propagate to form the shell layer. At the low grafting efficiency (4-8 h), the natural rubber seed particle was a compact packing of St/GMA particles. When the grafting efficiency increased (10 h), the St/GMA particles enhanced the encapsulation of the core and then fused to give a shell layer with smooth surface. It clearly shows that increasing the grafting efficiency gave thicker poly (styrene-co-glycidyl methacrylate) shells around natural rubber cores.

4.5 Characterization of Grafted Natural Rubber

4.5.1 Functional Groups in the Grafted Natural Rubber

The functional groups in the natural rubber and the grafted natural rubber were investigated by FT-IR. The FT-IR spectra in the region of 4000-400 cm^{-1} for natural

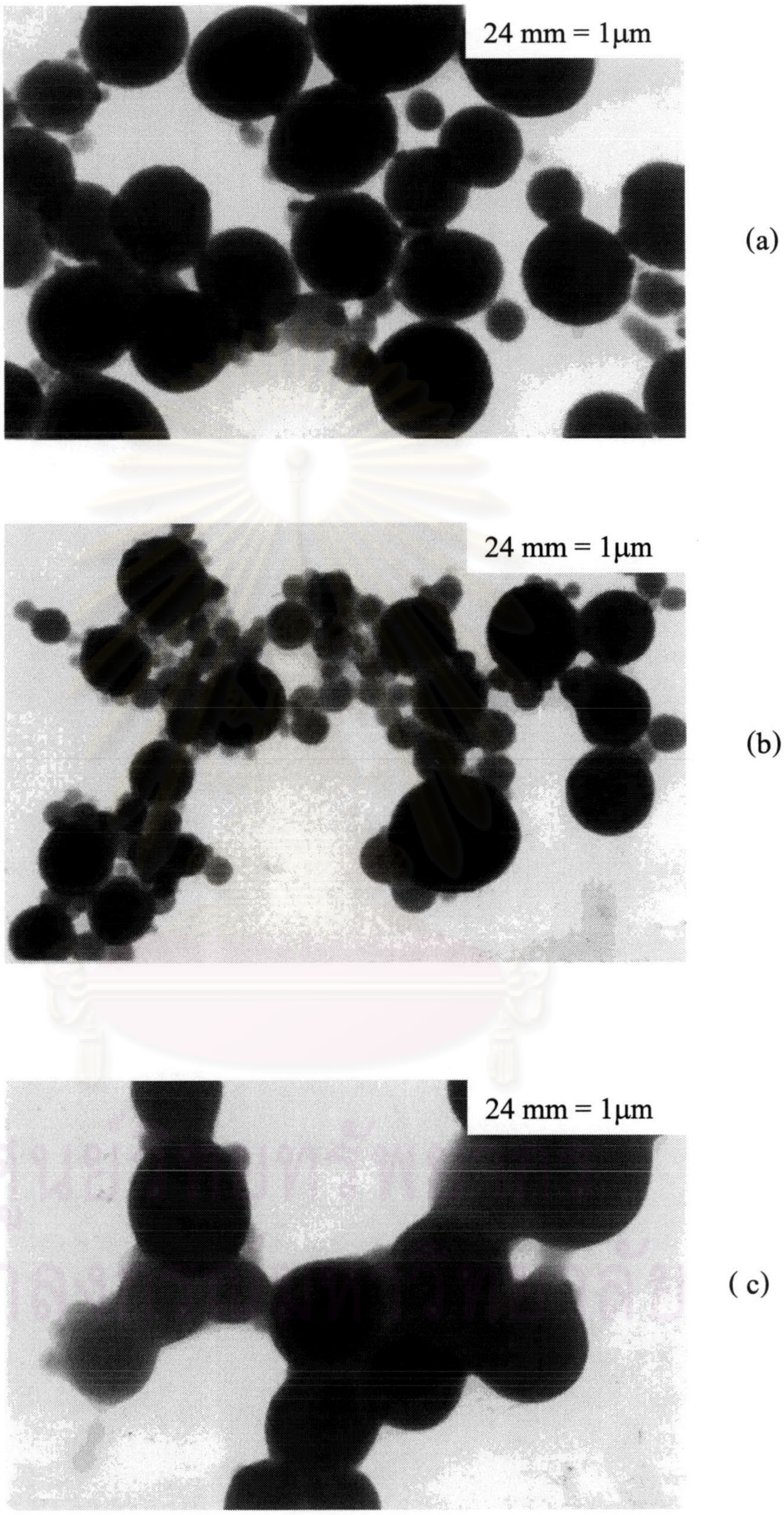


Figure 4.8 Transmission Electron Micrographs of the Particle Morphologies of Grafted Natural Rubber : (a) 4 h, (b) 8 h, and (c) 10 h (x24000)

rubber and grafted natural rubber were shown in Figures 4.9 and 4.10. The FT-IR spectra of natural rubber exhibited the characteristic absorption bands of C=C stretching vibration at 1460 cm^{-1}, the C-H stretching vibration at 1371 cm^{-1}, the C-C stretching vibration at 1235 cm^{-1} and the C=C bending vibration at 853 cm^{-1} [29]. The new peaks in FT-IR spectra of grafted natural rubber show absorption band of O-H stretching vibration at 3371 cm^{-1}, the C-H stretching vibration of aromatic ring at 3040 cm^{-1}, the C=O stretching vibration of glycidyl methacrylate at 1738 cm^{-1}, the C=C stretching vibration of aromatic ring of styrene at 1494 cm^{-1}, epoxy group of glycidyl methacrylate at 929 cm^{-1} and C=C-H bending of aromatic ring at 695 cm^{-1}[22]. This confirms the occurance of grafting of styrene and glycidyl methacrylate onto natural rubber.

4.5.2 Functional Groups in the Samples After Solvent Extraction

The FT-IR spectra of petroleum ether extract and acetone extract were shown in Figures 4.12 and 4.13. The schematic experimental process is summarized in Figure 4.11. The FT-IR spectra of petroleum ether extract exhibited the characteristic absorption band of C=C stretching vibration at 1464 cm^{-1}, the C-H stretching vibration in aliphatic at 1371 $cm^{-1}$and the C=C bending vibration at 835 cm^{1}. The FT-IR spectra of acetone extract exhibited the characteristic absorption band of O-H stretching vibration at 3373 cm^{-1}, C=O stretching vibration of glycidyl methacrylate at 1733 cm^{-1}, C=C stretching vibration of aromatic ring of styrene at 1453 cm^{-1}, the C-C stretching vibration at 1173 cm^{-1}, and C=C-H bending of aromatic ring of styrene at 703 cm^{-1}. This confirms that petroleum ether extracted free natural rubber and acetone extracted free homopolymer (St/GMA) from grafted natural rubber.

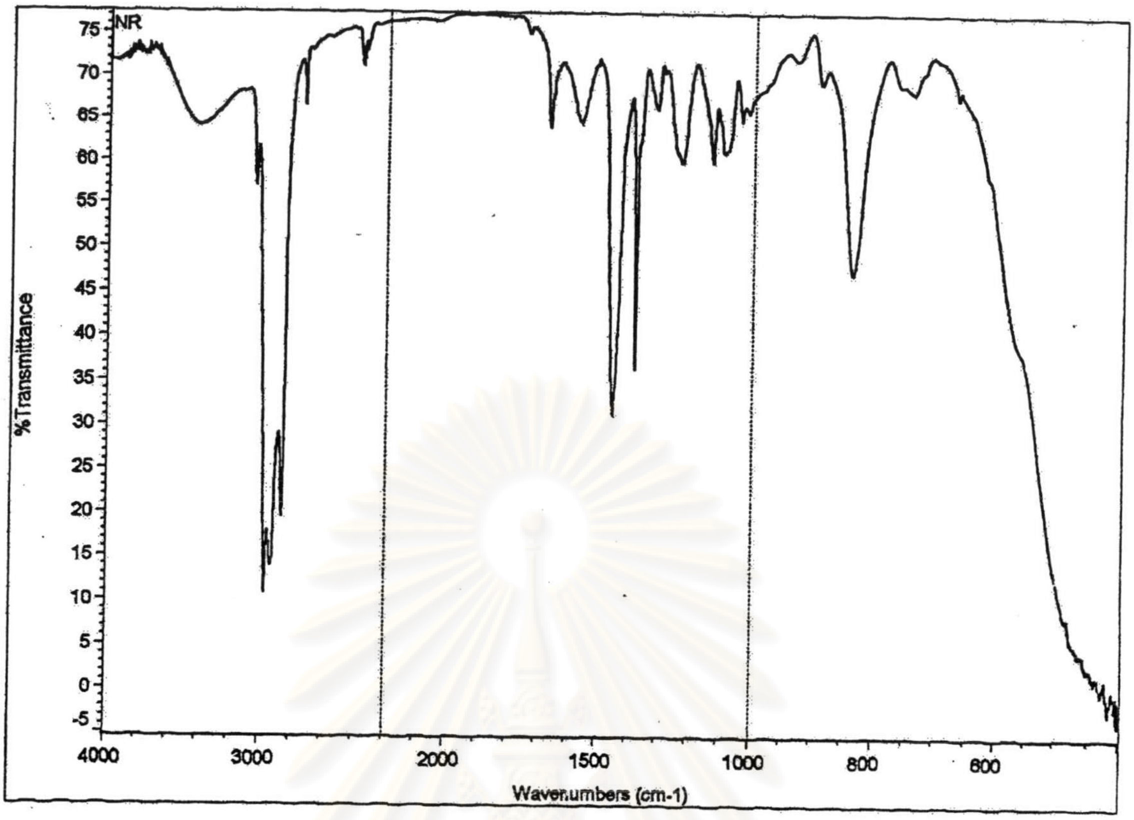


Figure 4.9 The FT-IR Spectrum of Natural Rubber

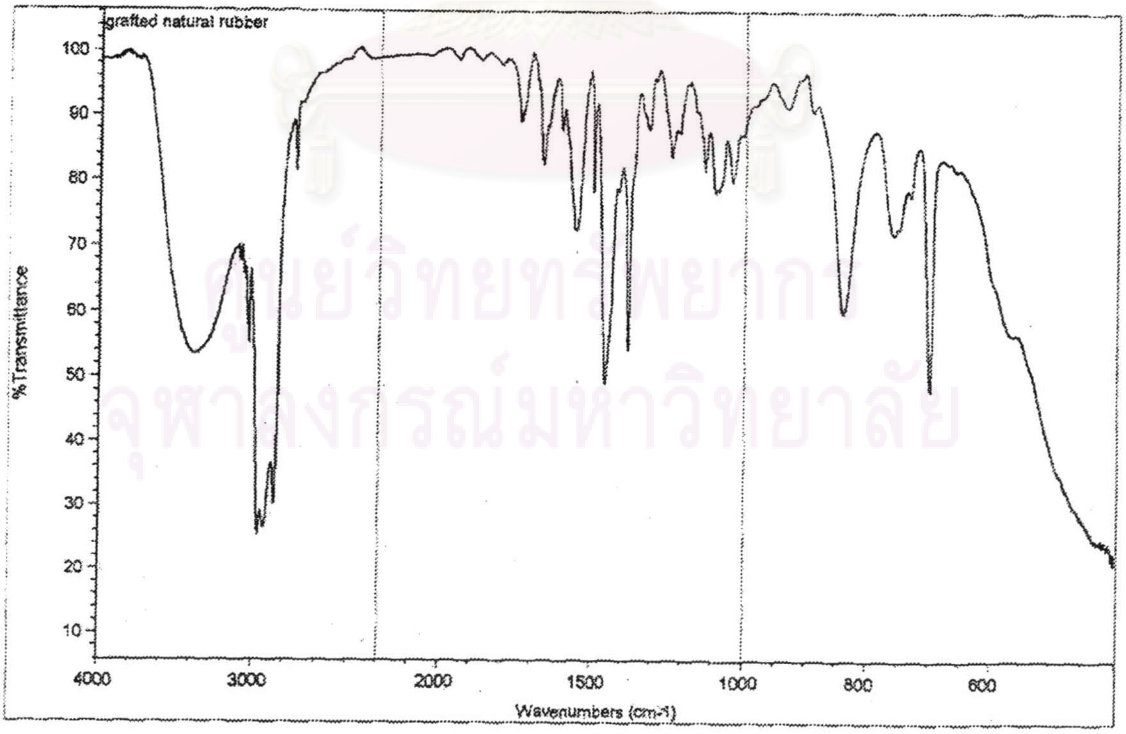


Figure 4.10 The FT-IR Spectrum of Grafted Natural Rubber

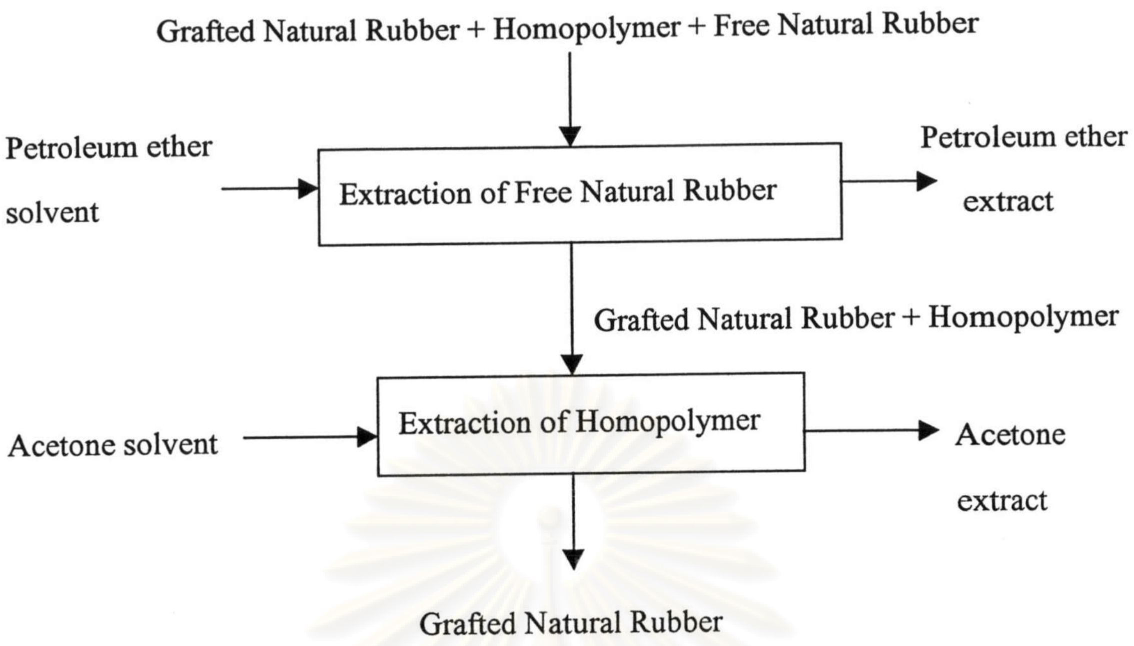


Figure 4.11 The Schematic Experimental Process of Samples After Solvent Extraction

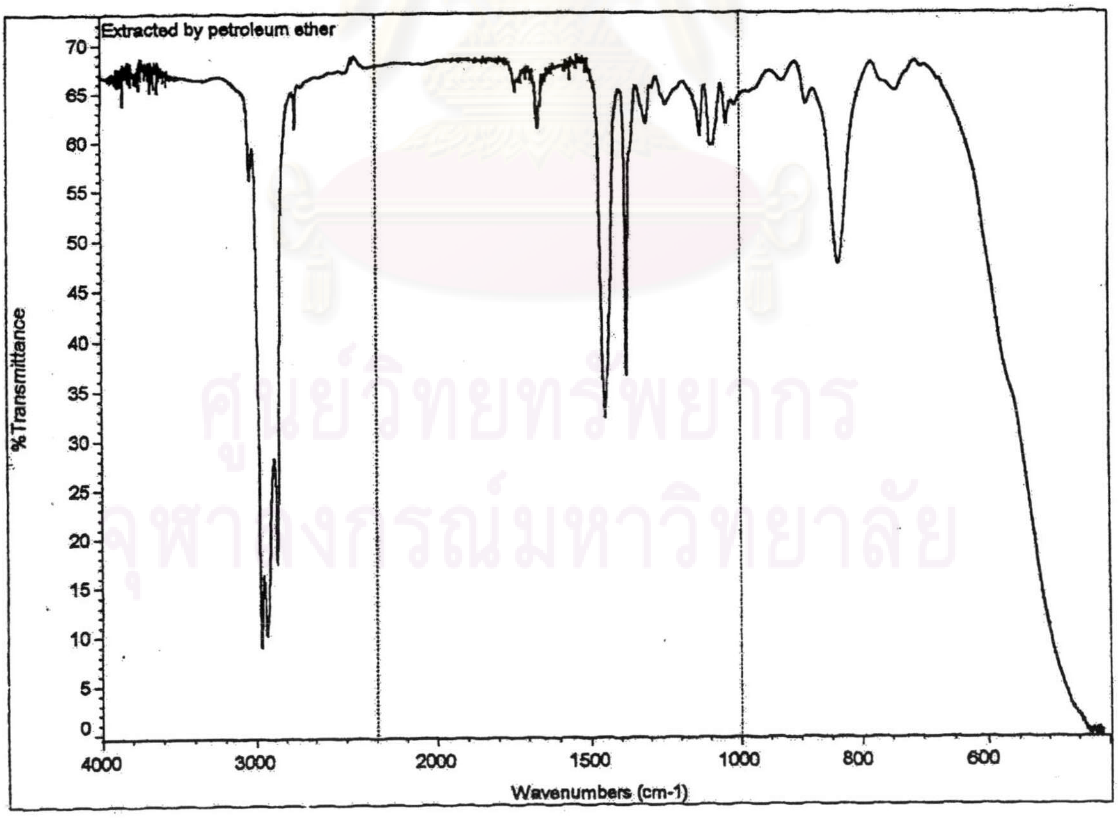


Figure 4.12 The FT-IR Spectrum of Petroleum Ether Extract

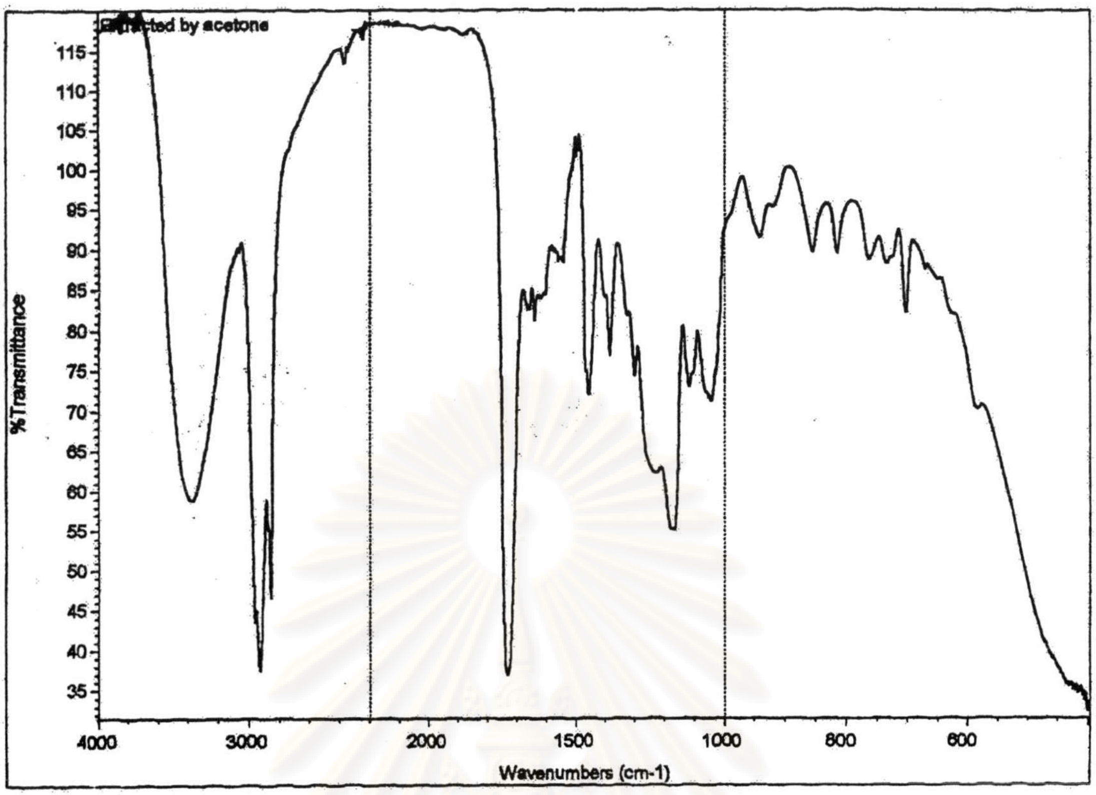


Figure 4.13 The FT-IR Spectrum of Acetone Extract

4.5.3 NMR Spectroscopy

The grafted natural rubber were dissolved with $CDCl_3$. The copolymer composition of grafted natural rubber were determined by ^{1}H-NMR and ^{13}C-NMR spectra. From Figure 4.14, The ^{1}H-NMR spectrum of grafted natural rubber revealed the signals between δ_H 6.4 to δ_H 7.1 ppm belonged to aromatic protons, the signal at δ_H 5.1 ppm belonged to olefinic protons, the signal at δ_H 3.5 ppm belonged to -C$\underline{H}$-Ph, and the signals between δ_H 1.7 to δ_H 2.0 ppm belonged to all aliphatic protons. From Figure 4.15, The ^{13}C-NMR spectrum of grafted natural rubber indicated the important carbon signals which could be assigned as follows : the signals at δ_C 47 and δ_C 44 ppm referred to carbon of epoxy group of glycidyl methacrylate. The signals at δ_C 63 and δ_C 73 ppm referred to the aliphatic group of –$\underline{C}H_2$-OH and –$\underline{C}$H-OH, respectively. This confirmed that the epoxy group of glycidyl methacrylate was opened. The signals between δ_C 124 to δ_C 136 ppm referred to aromatic region of styrene and isoprene, and the signal at δ_C 176 ppm referred to carbonyl group of glycidyl methacrylate. The above information confirms the occurance of grafting styrene and glycidyl methacrylate onto natural rubber.

From FT-IR and NMR spectrum, it clearly confirms that some of epoxy group of glycidyl methacrylate was broken by water and potassium hydroxide. So the grafted natural rubber contained glycidyl methacrylate with epoxy group and some glycidyl methacrylate which epoxy group was broken.

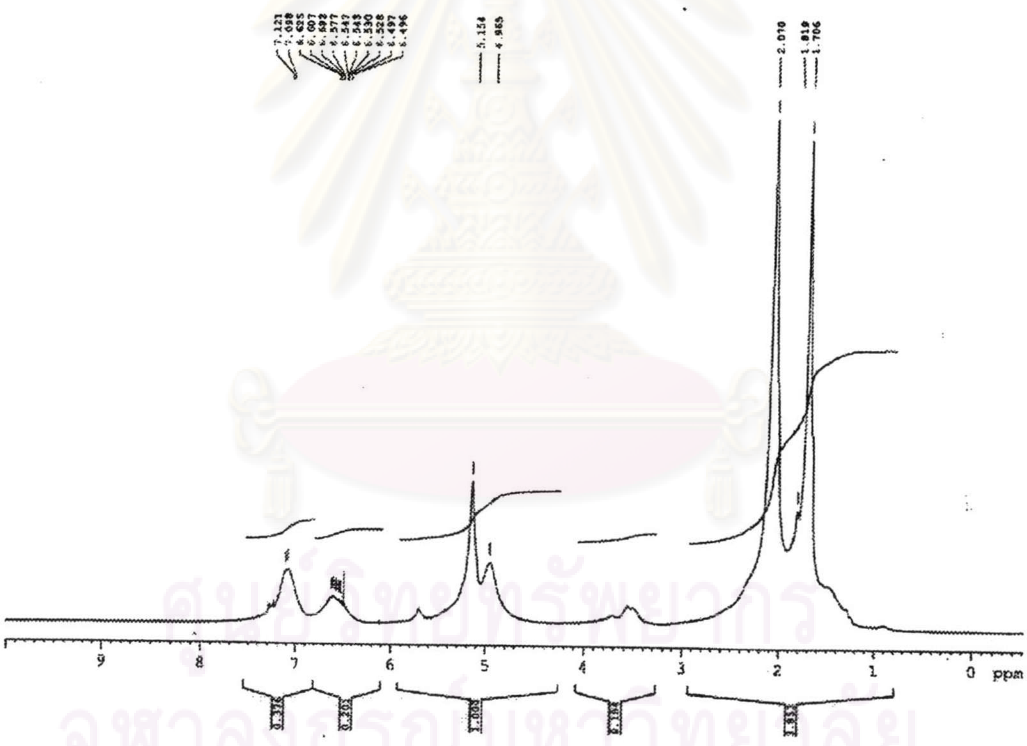


Figure 4.14 The ^{1}H-NMR Spectrum of Grafted Natural Rubber (Experimental Condition : DPX-400, 400 MHz)

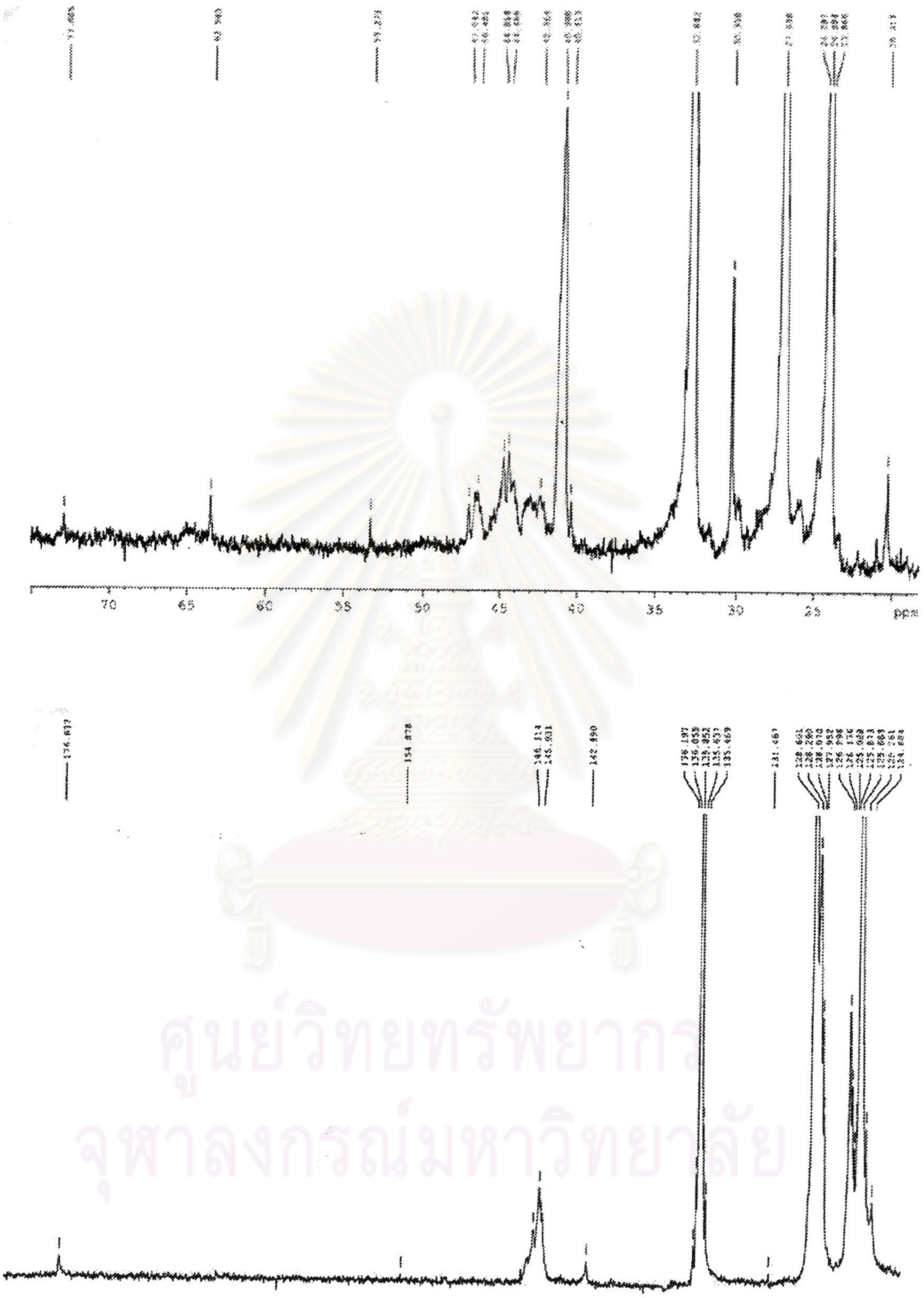


Figure 4.15 The ^{13}C-NMR Spectrum of Grafted Natural Rubber (Experimental Condition DPX-400, 400 MHz)

4.5.4 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis is another important way to characterize the graft copolymer. The Parallel Plate mode was used to determine the dynamic mechanical properties of the grafted natural rubber of different monomer concentrations at temperature range of –80 to +20°C, heating rate of 5°C min^{-1} and frequency of 1 Hz.

The effect of monomer concentration on the value of tanδ and glass transition temperature are shown in Table 4.6. The tanδ is defined as the ratio of loss modulus to storage modulus. The glass transition temperature was taken as the temperature at which the loss factor tanδ reached a maximum. From Figure 4.16, it can be seen that tanδ showed the maximun values around the transition region. It is apparent that the large energy loss peak were associated with the large changes in the modulus. The high energy input was used for joint motion of parts of the main polymer chains in the transition region. The tanδ peak became clearly more broaden with decreasing monomer concentration in grafted natural rubber. This indicated the greater dynamic losses. The losses could be due to more mechanical energy input converted to heat generated during the deformation and more energy losses in the movements of the polymer chain. The glass transition temperature and tanδ of grafted natural rubber decreased with increasing monomer concentration in grafted natural rubber. It can be explained that the rubber chain was more immobilized due to the higher monomer amount grafted.

Figure 4.17 shows the dependence of the storage modulus on temperature for the grafted natural rubber prepared from different monomer concentration (50, 100, and 150 phr). It should be noted that the mode used was not able to determine the absolute values of loss or storage modulus. In this case, the storage modulus decreases with increasing temperature. This is due to the relaxations arising from local motions of the polymer chain which is stiff around the transition region. The storage modulus increases with increasing monomer concentration. The increase in storage modulus can be explained that the monomer addition generally results in an increase of the stiffness of the grafted natural rubber. This also contributed to the improved mechanical properties.

Table 4.6 Glass Transition Temperature and tanδ of the Grafted Natural Rubber by DMTA Technique

Grafted Natural Rubber	Tg (°C)	tanδ
Natural rubber	-48.0	1.249
Monomer 50 phr	-49.3	0.573
Monomer 100 phr	-54.2	0.582
Monomer 150 phr	-59.0	0.387

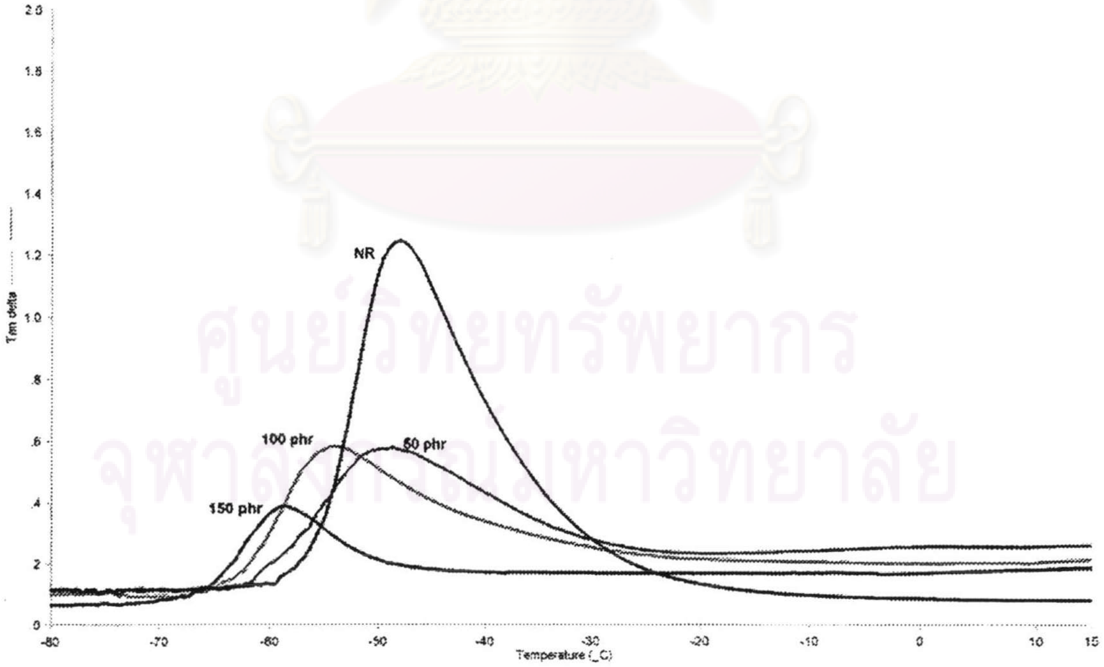


Figure 4.16 Loss Factor (tanδ) of the Grafted Natural Rubber at Different Monomer Concentration

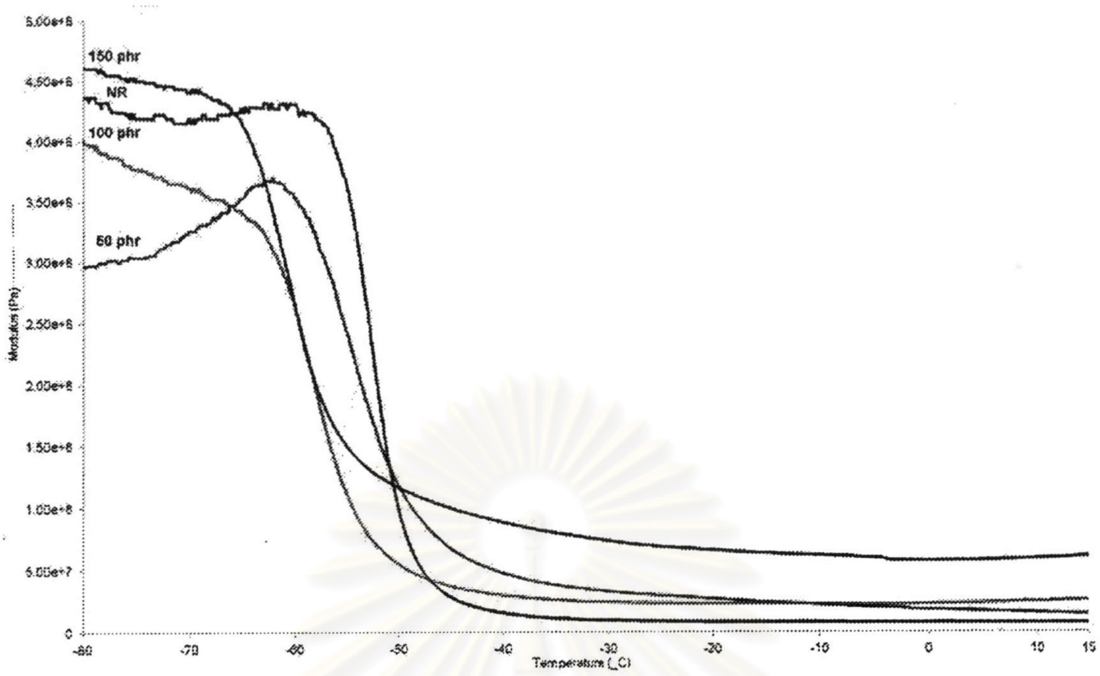


Figure 4.17 Storage Modulus of Grafted Natural Rubber at Different Monomer Concentration

4.6 Mechanical Properties of the STR5L Blends with PMMA and Grafted Natural Rubber as a Compatibilizer

The properties of STR5L and PMMA pellet (MF#001) are presented in Tables 4.7 and 4.8. In this work, the graft copolymer of styrene and glycidyl methacrylate onto natural rubber was carried out at 60°C for 10 h and the grafted natural rubber with monomer 100 phr was selected for the preparation of the blends. The grafted natural rubber had percentage grafted natural rubber of 71.8 and grafting efficiency of 69.3. The blends were prepared at blending ratios of STR5L to PMMA of 70/30 and 50/50, together with various quantities of grafted natural rubber (0, 5, 10, 15 and 20 phr). The mechanical properties of unvulcanized and vulcanized blends were investigated. The tensile properties, tear strength, hardness and impact energy of the blends are shown in Tables 4.9 and 4.10 and Figures 4.18 and 4.19.

a) Tensile properties

From Tables 4.9 and 4.10, the STR5L/PMMA blends without grafted natural rubber has a low tensile strength. The tensile strength of blend was improved by the addition of grafted natural rubber. From Figure 4.18a for unvulcanized STR5L/PMMA blends at ratio of 70/30, the tensile strength increases with increasing the grafted natural rubber content and slightly decreases at grafted natural rubber content above 10 phr. For unvulcanized STR5L/PMMA blends at ratio of 50/50, tensile strength increases and reaches a leveling off at 5 phr of the grafted natural rubber content. This results were the same as the vulcanized STR5L/PMMA blends. The decreases in tensile strength may be due to excessive crosslink density of the blends or may be due to the interfacial saturation. Thomas and Prud'homme reported on the so-called interfacial saturation of binary polymer blends by the addition of a compatibilizer. The presence of the graft copolymer reduces the domain size considerably and the polydispersity is reduced. The reduction in domain size and increase in tensile strength continue until the interface is saturated. The saturation of the interface is indicated by the leveling-off of the domain size and tensile properties [18]. The tensile strength of unvulcanized STR5L/PMMA blends at ratio of 70/30 were higher than that of the blend at ratio of 50/50. For STR5L/PMMA blends at ratio of 70/30, the PMMA is dispersed in the continuous STR5L as a domains. For STR5L/PMMA blends at ratio of 50/50, the blends had the influence of STR5L as well as of PMMA; consequently, the tensile strength of the blends decreases because of the brittle property of thermoplastic of PMMA. From Figure 4.19a, tensile strength of the vulcanized STR5L/PMMA blends at ratio of 50/50 was higher than that blend at ratio of 70/30. The crosslinking of the molecules with sulphur would retain the elasticity and decrease the plasticity of the blends.

Table 4.7 The Properties of STR5L

Parameter	Value
Dirt (max.) %wt.	0.014
Ash (max.) %wt.	0.250
Nitrogen (max.) %wt.	0.400
Volatile Matter (max.) %wt.	0.620
Initial Plasticity	42.0
PRI Index	83.2
Colour Lovibond Scale (individual value, max.)	7.0
Mooney Viscosity	90.64

(Data from test method of Standard Thai Rubber)

Table 4.8 Typical Data of PMMA (Crystallite MF#001)

Properties	Value
Specific Gravity	1.19
Refractive Index Nd	1.49
Melt flow rate (230°C /3.8 kgs.)	14.0
Thermal Specific Heat	0.35
Coefficient of Linear Thermal Expansion	6×10^{-5}
Coefficient of Thermal Conductivity	5×10^{-4}
Heat Distortion Temperature	83°C (182°F)
Water Absorption	0.3

(Data from TPI Polyacylate Co.,Ltd.)

From Tables 4.9 and 4.10, tensile strength of vulcanized STR5L/PMMA blends at ratio of 70/30 and 50/50 were higher than that of unvulcanized blends. During vulcanization, the long chains of the rubber molecules were crosslinked by reactions with the vulcanizing agent to form three dimentional structures. This crosslink reaction transforms the soft weak plastic-like material into a strong elastic product.

From Figures 4.18b and 4.19b, elongation at break of STR5L/PMMA blends also increases with increasing amounts of grafted natural rubber content and then decreases. The elongation at break of unvulcanized and vulcanized STR5L/PMMA blends at ratio of 70/30 was higher than that of blend at ratio of 50/50 for all grafted natural rubber content. It may be due to the influence of PMMA (brittle thermoplastic) which caused the decrease in the elongation at break.

b) Tear Strength

From Figures 4.18c and 4.19c, tear strength increases with increasing grafted natural rubber content and further addition at above 10 phr of grafted natural rubber content makes only a little change in the tear strength. Similar to the tensile strength, the leveling off in tear strength was observed for STR5L/PMMA blend at ratio of 70/30 with 10 phr of grafted natural rubber content and STR5L/PMMA blend at ratio of 50/50 with 5 phr of grafted natural rubber content . The change in tear strength of the blends can be explained in terms of the morphology of the system. Addition of the grafted natural rubber may reduce the size of the dispersed PMMA. The distribution of particles also becomes uniform. The reduction in particle size is due to the reduction in interfacial tension and the increase of interfacial adhesion. This would inhibit the propagation of a growing crack during tearing. Hence, the grafted natural rubber as a compatibilizer enhances the resistance to tear and the leveling off in tear strength of STR5L/PMMA blends at 5 phr and 10 phr of grafted natural rubber content is also due to the interfacial saturation.

Table 4.9 Properties of Unvulcanized STR5L/PMMA Blends

	70/30 ratio of STR5L/PMMA blends					50/50 ratio of STR5L/PMMA blends				
Grafted natural rubber content, (phr)	0	5	10	15	20	0	5	10	15	20
- Tensile strength, (MPa)	0.58	1.16	2.94	2.06	1.85	1.65	2.24	1.56	1.39	1.14
- Elongation at break, (%)	64	232	142	260	202	6.90	6.61	6.85	7.33	7.27
- Stress@ 100% modulus, (MPa)	0.56	1.02	2.78	1.64	1.60	-	-	-	-	-
- Tear strength (N/mm)	8.16	10.3	14.0	14.2	12.5	14.9	14.3	19.0	17.9	19.0
- Hardness (Shore A)	43.4	45.1	64.8	58.0	49.0	81.3	85.2	90.1	86.6	77.9
- Impact energy (J)	-	-	-	-	-	0.22	0.25	0.26	0.31	0.34

Table 4.10 Properties of Vulcanized STR5L/PMMA Blends

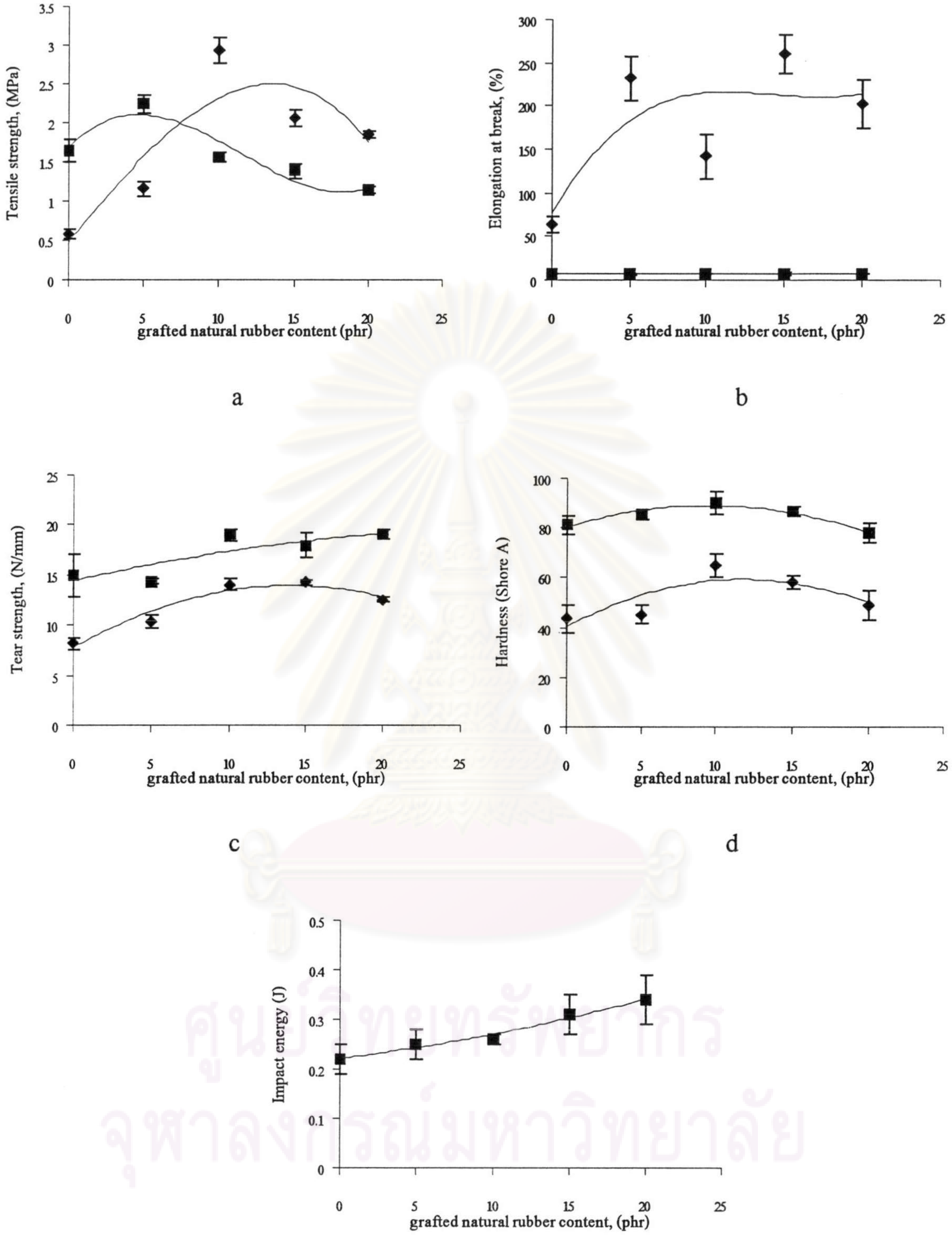
	70/30 ratio of STR5L/PMMA blends					50/50 ratio of STR5L/PMMA blends				
Grafted natural rubber content, (phr)	0	5	10	15	20	0	5	10	15	20
- Tensile strength, (MPa)	1.63	2.39	3.64	2.56	2.62	2.98	4.62	3.97	3.83	2.65
- Elongation at break, (%)	478	716	681	492	351	11.4	20.2	30.6	28.0	26.9
- Stress@ 100% modulus, (MPa)	0.65	0.63	0.89	0.89	1.08	1.33	2.02	1.39	1.33	-
- Tear strength (N/mm)	13.5	16.1	18.2	17.8	16.9	17.6	21.5	19.6	16.1	13.1
- Hardness (Shore A)	48.7	41.4	50.0	45.8	40.0	69.6	70.4	74.4	68.3	62.5

c) Hardness

Hardness, as applied to rubber, may be defined as the resistance to indentation under conditions which do not puncture the rubber [2]. From Figures 4.18d and 4.19d, the hardness of unvulcanized STR5L/PMMA blends at ratio of 50/50 increases with increasing the percentage grafted natural rubber content and then decreases. This similar results were also observed for vulcanized STR5L/PMMA blends. The hardness of STR5L/PMMA blends at ratio of 50/50 were higher than that of blends at ratio 70/30. The hardness of vulcanized STR5L/PMMA blends were lower than that of unvulcanized STR5L/PMMA blends. This suggest that the compatibility of grafted natural rubber with STR5L/PMMA blends was increased by adding the vulcanizing compound. Therefore, the vulcanizing compound caused the rubber chain branching and flexible and the hardness of the vulcanized blends decreased.

d) Impact Energy

From Figure 4.18e, the impact energy of STR5L/PMMA blends at ratio of 50/50 increases with increasing grafted natural rubber content. At 20 phr of grafted natural rubber, the impact energy reaches maximum value of 0.35 J. The increase in grafted natural rubber content make the crack propagation more difficult, leading to the increased impact energy.



a

b

c

d

e

Figure 4.18 Effect of Grafted Natural Rubber Content on the Mechanical Properties of Unvulcanized STR5L/PMMA Blends : (◆) 70/30 ratio; (■) 50/50 ratio

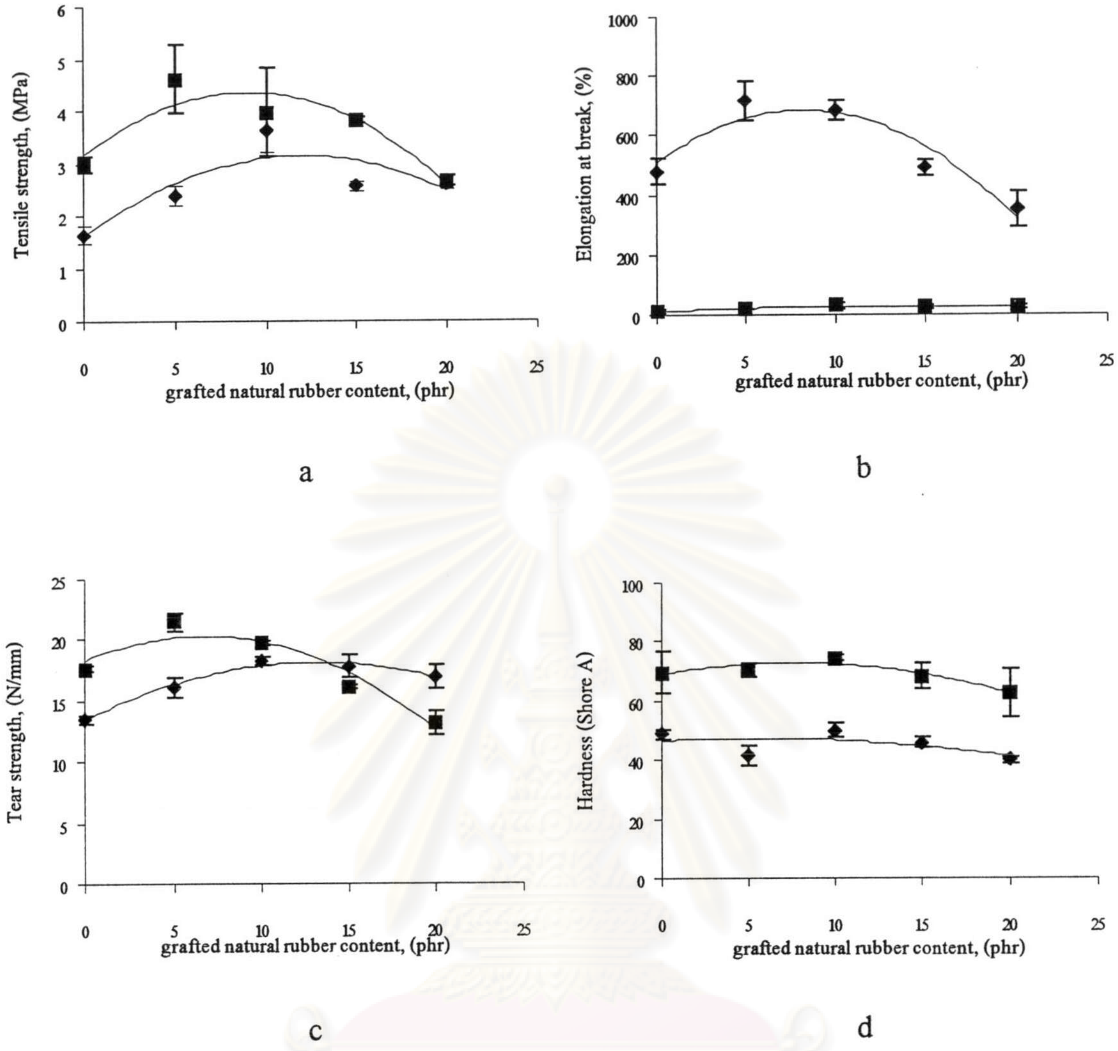


Figure 4.19 Effect of Grafted Natural Rubber Content on the Mechanical Properties of Vulcanized STR5L/PMMA Blends : (◆) 70/30 ratio; (■) 50/50 ratio

4.7 Oil Absorption

Oil absorption of vulcanized STR5L/PMMA blends at ratio of 70/30 and at ratio of 50/50 were reported as percentage weight change. The percentage of weight change with various grafted natural rubber content is shown in Table 4.11 and Figure 4.20. The detail of all data and the calculation are shown in Appendix D.

Table 4.11 The Percentage of Weight Change of Vulcanized STR5L/PMMA Blends

	% Weight change of vulcanized STR5L/PMMA blends				
Grafted natural rubber content, (phr)	0	5	10	15	20
At ratio of 70/30	21.0	24.8	20.9	20.5	24.4
At ratio of 50/50	16.0	14.4	14.2	18.1	19.5

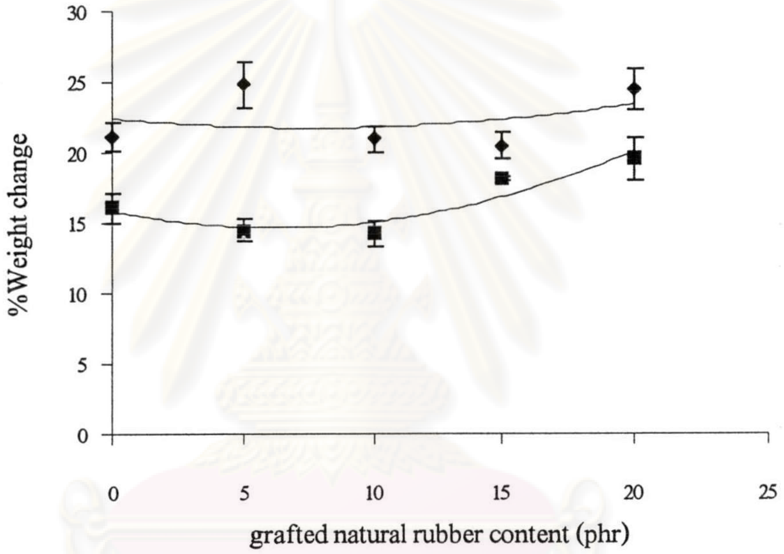


Figure 4.20 The Percentage of Weight Change of Vulcanized STR5L/PMMA Blends : (◆) 70/30 ratio; (■) 50/50 ratio

The vulcanized STR5L/PMMA blends at ratio of 70/30 absorbed more oil than that at ratio of 50/50. The percentage of weight change in vulcanized STR5L/PMMA blends at ratios of 70/30 and 50/50 did not change much with increasing grafted natural rubber content. The increase in PMMA content and grafted natural rubber content may increase the polarity of the blends. The blends exhibit the resistance to oil absorption (non-polar oil).

4.8 Mechanical Properties of the Grafted Natural Rubber/PMMA Blend.

The tensile properties, tear strength and hardness of NR-g-St/GMA/PMMA blend and NR-g-MMA60/PMMA blend are shown in Table 4.12 and Figure 4.21. NR-g-St/GMA was prepared at 60°C, monomer (St/GMA) 100 phr for 10 h. NR-g-MMA60 was prepared at 55°C, monomer (MMA) 60 phr for 8 h.

Table 4.12 Properties of Grafted Natural Rubber/PMMA Blends

	NR-g-St/GMA/PMMA blends				NR-g-MMA60 phr/PMMA blends[19]			
	100/0	70/30	60/40	50/50	100/0	70/30	60/40	50/50
- Tensile strength, (MPa)	0.48	2.80	3.37	5.50	3.50	4.10	5.30	8.10
- Elongation at break, (%)	776.5	145.3	12.8	7.70	410.1	105.7	21.7	20.4
- Stress@ 100% modulus, (MPa)	0.15	2.64	-	-	1.7	4.1	-	-
- Tear strength (N/mm)	6.63	17.34	17.51	23.09	13.20	15.50	16.30	25.00
- Hardness (Shore A)	16.5	65.5	84.4	90.7	15.0	21.6	35.8	47.8

a) Tensile Properties

From Table 4.12 and Figure 4.21a, the tensile strength of NR-g-St/GMA/PMMA blends and NR-g-MMA60/PMMA blends increase with increasing PMMA content. For NR-g-MMA60/PMMA blends, the tensile strength was higher than NR-g-St/GMA/PMMA blends. The comparison of the mechanical properties of NR-g-MMA60 and NR-g-St/GMA suggested that NR-g-MMA60 is more compatible to PMMA than NR-g-St/GMA. However NR-g-St/GMA could increase the tensile strength of the blends. From Figure 4.21b, the elongation at break of NR-g-St/GMA/PMMA blends and NR-g-MMA60/PMMA blends decreased with increasing PMMA content due to the presence of PMMA component (the brittle thermoplastic, low strain at break). The elongation at break of NR-g-MMA60/PMMA blends was less than NR-g-St/GMA/PMMA blends.

b) Tear strength

The tear strength considerably increases with increasing content of PMMA as shown in Figure 4.21c. Tear strength of NR-g-MMA60/PMMA blends were higher than NR-g-St/GMA/PMMA blends. The increase of MMA content may cause the increase of the hard segment of MMA grafted chain and PMMA homopolymer. The distribution of particles also become uniform and enhances the resistance to tear.

c) Hardness

From Figure 4.21d, PMMA can enhance the hardness properties. The hardness increased with increasing PMMA content in NR-g-MMA60/PMMA and NR-g-St/GMA/PMMA blends. The hardness of NR-g-St/GMA/PMMA blends was higher than NR-g-MMA60 phr/PMMA blends. This is due to the fact that styrene and glycidyl methacrylate segment increses the hardness of the blends.

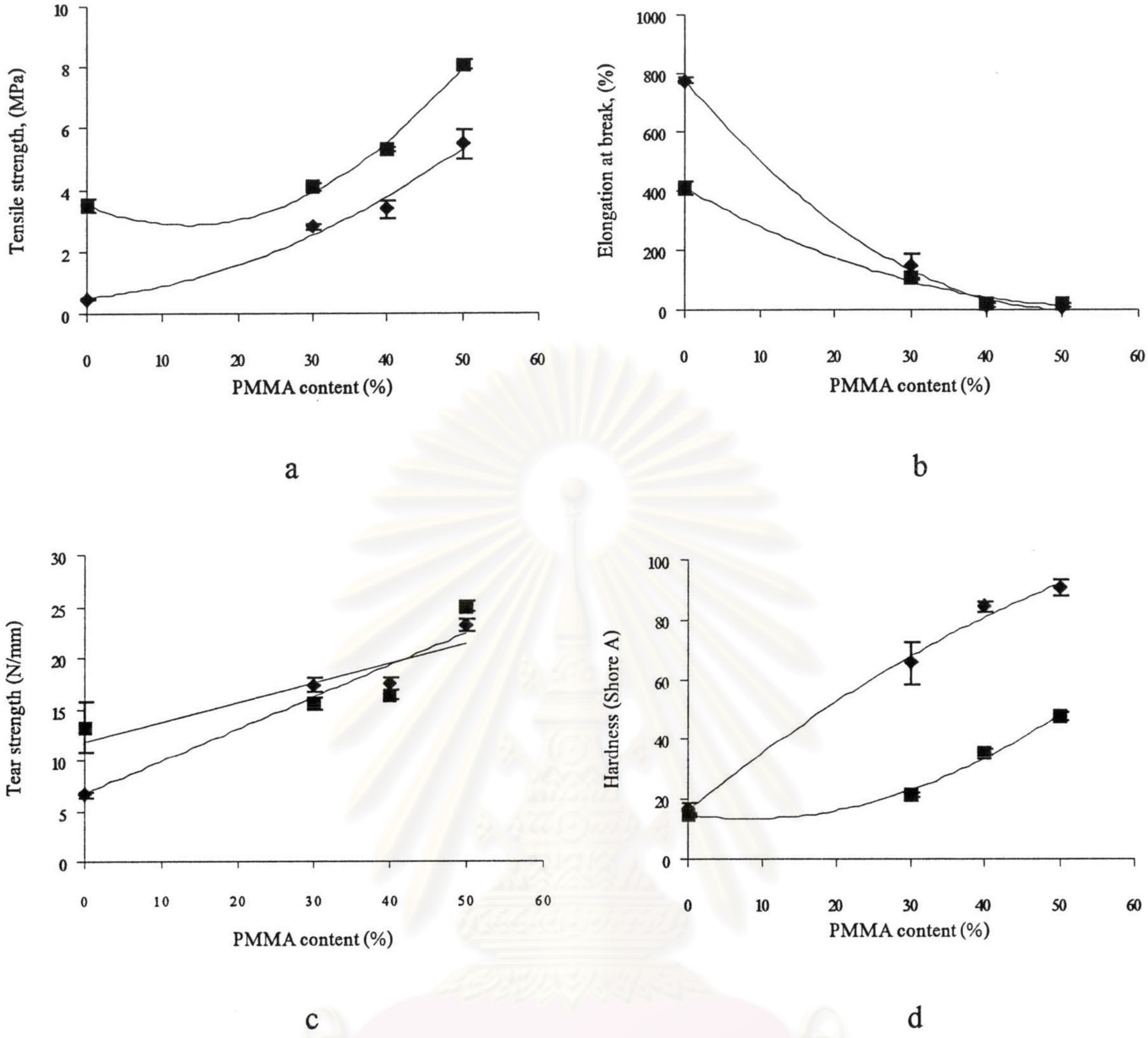


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Figure 4.21 Effect of PMMA Content on the Mechanical Properties of Grafted Natural Rubber/PMMA Blends : (◆), NR-g-St/GMA/PMMA Blends ; (■), NR-g-MMA60/PMMA Blends

4.9 Scanning Electron Microscopy (SEM)

The scanning electron microscope was employed to investigate the fracture surface of the specimen from the tensile properties test. The influence of grafted natural rubber as compatibilizer on the properties of unvulcanized and vulcanized STR5L/PMMA blends are shown in Figures 4.22-4.26.

Figures 4.22 and 4.23 show the tensile fracture surface of unvulcanized and vulcanized STR5L/PMMA blends at ratio of 70/30 with and without the graft copolymer. The fracture surface [Figure 4.22 (a) and Figure 4.23 (a)] of the uncompatibilized blends show no adhesion between the two phases. In the compatibilized blends [Figure 4.22 (b-c) and Figure 4.23 (b-c)], the dispersed domains are small in size and the area of contact is larger. The microfibrils between the matrix and the dispersed phase show signs of interfacial adhesion between the two phases. The grafted natural rubber acted as compatibizer in STR5L/PMMA blends because glycidyl methacrylate contains methacrylate groups as in the case of PMMA. Moreover, water and potassium hydroxide in emulsion polymerization can break epoxy group of glycidyl methacrylate which caused hydrogen bonding with carbonyl group of PMMA. These results were also confirmed by FT-IR and NMR. For the unvulcanized and vulcanized STR5L/PMMA blends at ratio of 50/50 (Figures 4.24 and Figure 4.25), the grafted natural rubber cause the good dispersion of PMMA in rubber phase. Therefore, the grafted natural rubber acted as compatibilizer could decrease the domain size of PMMA and the smooth fracture surface was observed.

From Figure 4.26, the SEM micrograph of NR-g-St/GMA/PMMA blends shows the increasingly finer structures of grafted natural rubber/PMMA blends obtained with increasing PMMA content. The cavitation of the specimen decreased with increasing of PMMA content, the higher grafted natural rubber content caused the increase of cavitation sites.

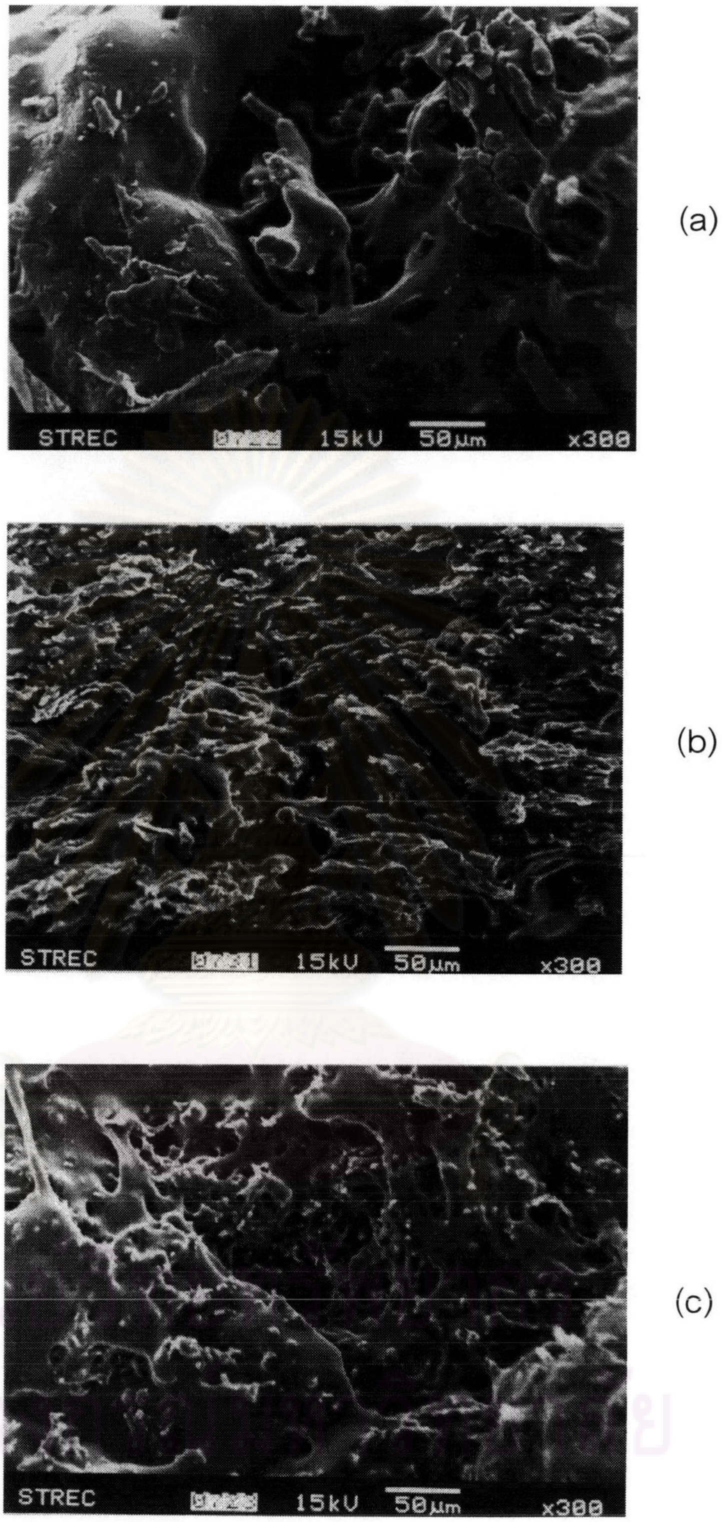

Figure 4.22 SEM Photographs of Unvulcanized of STR5L/PMMA Blends at ratio of 70/30 with Grafted Natural Rubber ; (a) 0 phr, (b) 10 phr, (c) 20 phr

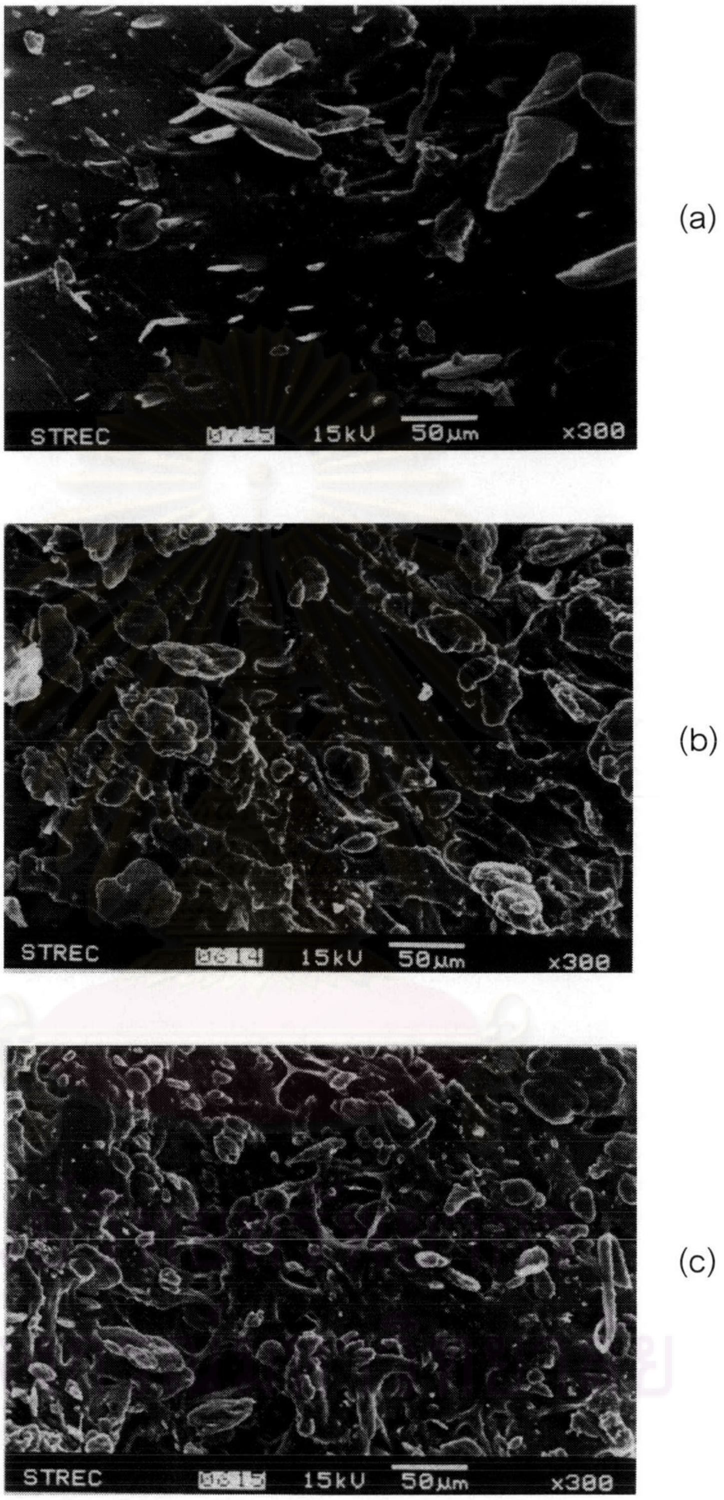

Figure 4.23 SEM Photographs of Vulcanized of STR5L/PMMA Blends at ratio of 70/30 with Grafted Natural Rubber ; (a) 0 phr, (b) 10 phr, (c) 20 phr

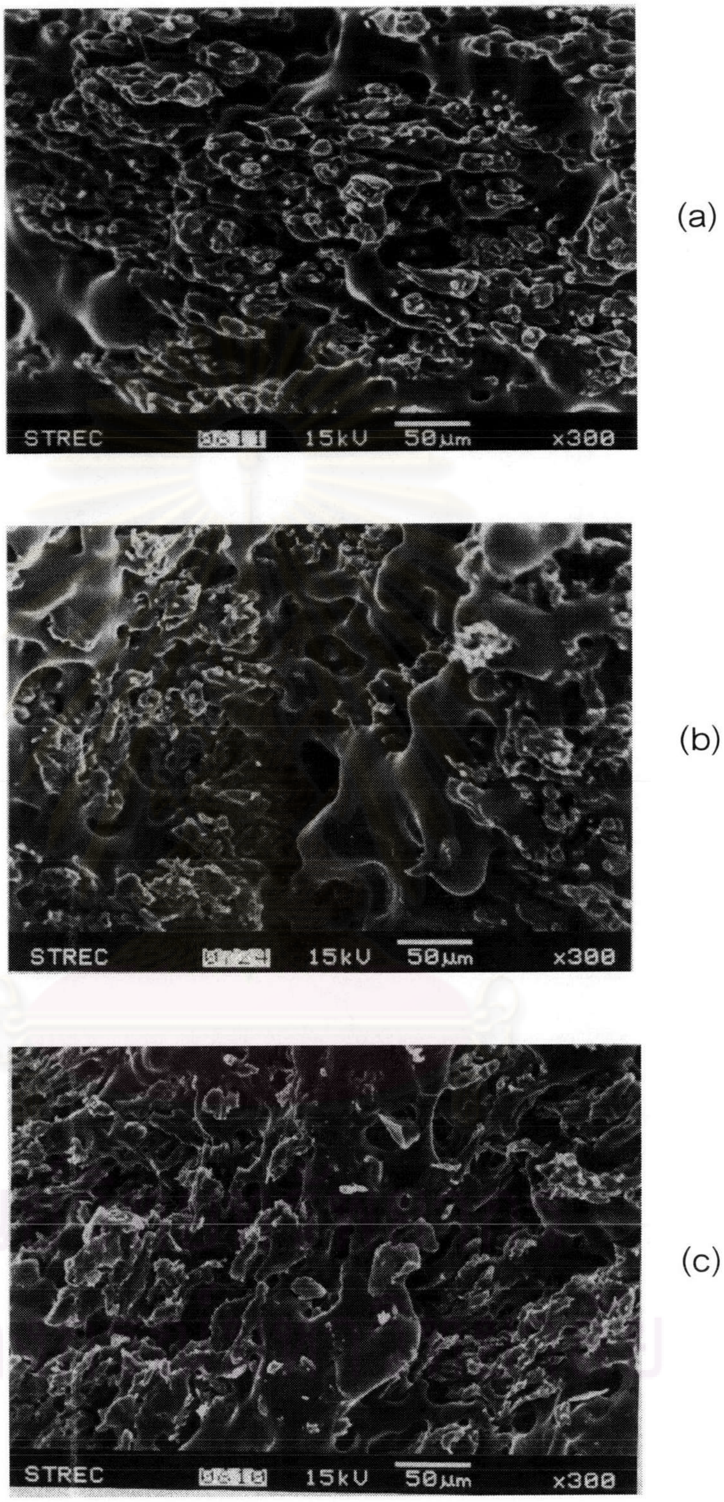

Figure 4.24 SEM Photographs of Unvulcanized of STR5L/PMMA Blends at ratio of 50/50 with Grafted Natural Rubber ; (a) 0 phr, (b) 5 phr, (c) 10 phr

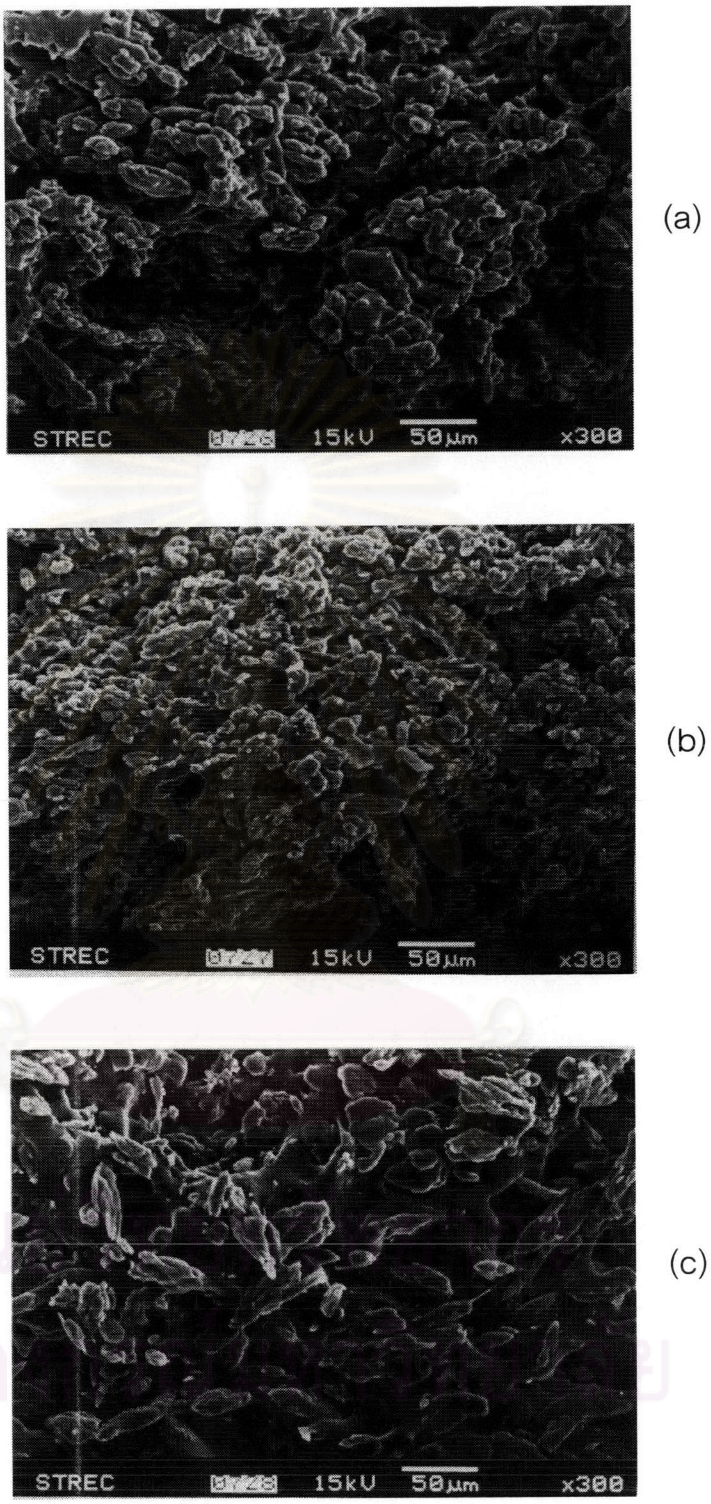

Figure 4.25 SEM Photographs of Vulcanized of STR5L/PMMA Blends at ratio of 50/50 with Grafted Natural Rubber ; (a) 0 phr, (b) 5 phr, (c) 10 phr

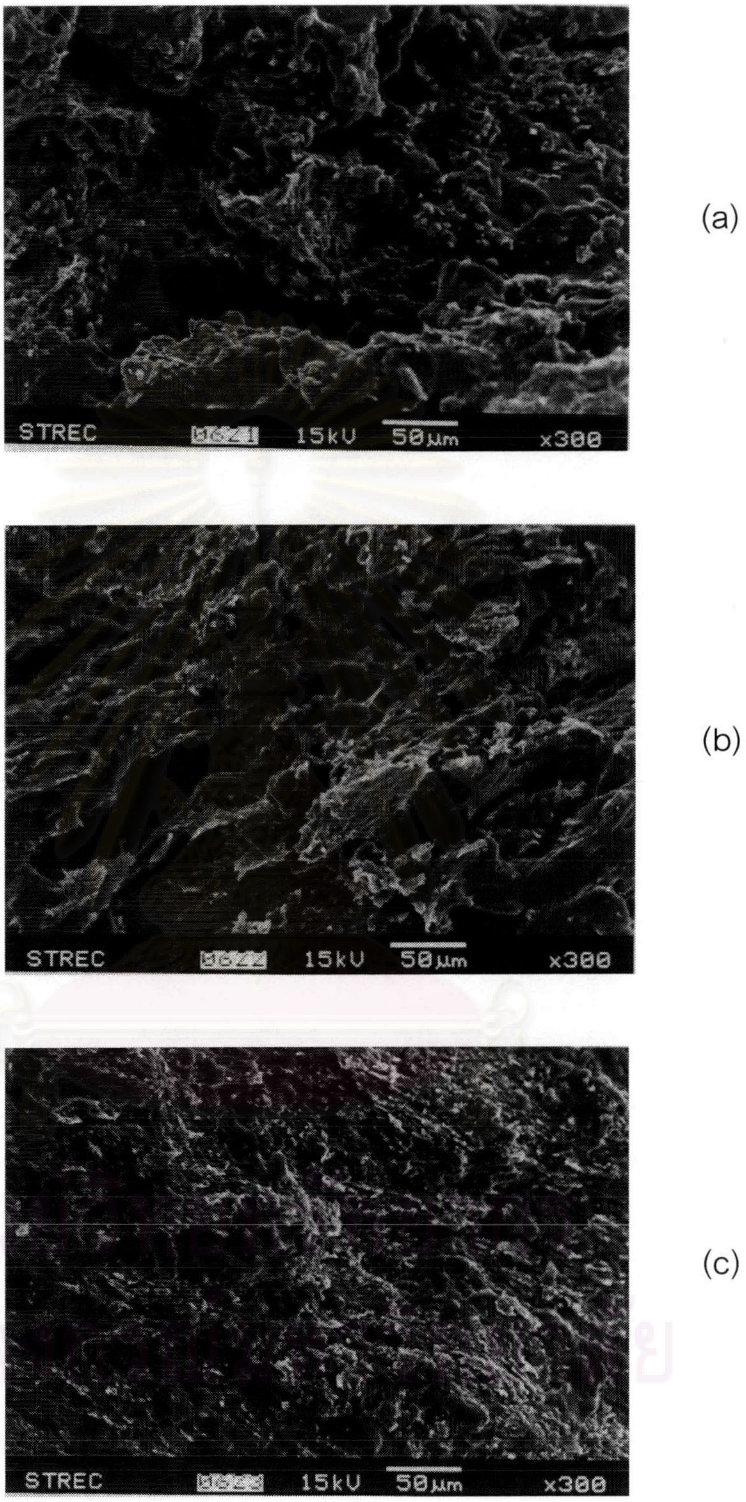

Figure 4.26 SEM Photographs of NR-g-St/GMA/PMMA Blends ; (a) 70/30, (b) 60/40, (c) 50/50