



## CHAPTER IV

### RESULTS AND DISCUSSION

The graft copolymerization of methyl methacrylate (MMA) onto natural rubber (NR) was prepared by seed emulsion polymerization. The graft product consisted of natural rubber (NR) core with poly(methyl methacrylate) (PMMA) acting as shell. To generate the sites for grafting, the selected initiator system composed with cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) has been used as redox initiators to generate radicals predominantly near the surface of the particle of NR latex (NRL), leading the formation of a layer of PMMA shell around the seed particle or domains of PMMA inside the seed particle (Lamb et al., 2001) as shown in Appendix C. Most of the free radicals of this initiator system produced at the interphase of swollen particle and water due to the solubility of CHPO is in the organic phase, with water-soluble TEPA used as the activator. (Wanvimon Arayapraneet et al., 2002). Mechanism of graft copolymerization is proposed in Appendix C. For the present study, the dielectric constants ( $\epsilon_r'$ ) of all chemicals used for graft copolymerization were measured to evaluate the potential of microwave absorption.

#### 4.1 Dielectric properties measurement of chemicals

Measurement of the dielectric properties of chemicals were done using open-ended coaxial line probes coupled with automated network analyzer (PUSCHNER, GERNAMY) and computer at the microwave frequencies from 1.6 to 2.6 GHz at 25°C as described in Chapter III and Figure 3.5. The dielectric properties of a material refer to the complex relative permittivity  $\epsilon_r^* = \epsilon_r' - j\epsilon_r''$ , where  $\epsilon_r'$  is the real relative permittivity, which is also known as the dielectric constant, whereas the imaginary part  $\epsilon_r''$  is the dielectric loss factor. The dielectric constant ( $\epsilon_r'$ ) is a measure of the ability of the material to be polarized or energy stored, while the loss factor ( $\epsilon_r''$ ) is a measure of the ability of the material to heat or energy loss by absorbing energy (Hassan et al., 2010). Table 4.1 shows dielectric properties of chemicals for graft copolymerization. Mostly, chemicals have a moderate dielectric

constant value except MMA and deionized (DI) water having higher dielectric constant as 7.89 and 37.83, respectively resulting from their high polar structures. For MMA, it is a polar molecule due to its acrylic functional group ( $\text{O}=\text{C}-\text{O}-\text{CH}_3$ ). Thus, MMA and DI water with good dielectric constants can absorb microwave energy higher than other chemicals. For the NR latex concentrate containing about 38% of water, the water molecules in the NR latex was loosely bound and easily aligned to the electric field. The dielectric properties of NR latex are mainly due to the orientations of water molecule and the geometrical shape of the molecule which is ellipsoidal. This suggests that the water molecules in the NR latex can be easily polarized resulting to absorb microwave energy as same as other chemicals. Non-rubber constituents do not contribute much to the dielectric properties of NR latex (Jayanthi and Sankaranarayanan, 2005; Hassan et al., 2010). Moreover, most chemicals have a good loss factor ( $\epsilon_r''$ ) value except the anionic surfactant sodium dodecylsulfate (SDS) and potassium hydroxide (KOH). This indicates that when these chemicals absorb the microwave energy, they can convert the microwave energy to heat energy. Although, SDS and KOH have low loss factor due to solid state, they can ionize in the water to become alkyl sulfate ion ( $\text{R}-\text{SO}_4^-$ ) and hydroxide ion ( $\text{OH}^-$ ), respectively, which can interact with the electromagnetic field of microwave energy to generate heat energy. When the heat occurred, the redox initiator was thermally ionized into the free radicals which might attack either the monomer or the NR molecule to produce monomer radicals ( $\text{M}^*$ ) and NR radicals ( $\text{NR}^*$ ), respectively, as active grafting sites for graft copolymerization. Furthermore, the microwave energy can also break carbon-carbon double bond of NR chain or MMA molecule to form  $\text{NR}^*$  and  $\text{M}^*$ , respectively.

**Table 4.1** Dielectric properties of chemicals for graft copolymerization

Chemicals	Dielectric constant ( $\epsilon_r'$ )	Loss factor ( $\epsilon_r''$ )
SDS (s)	1.41	0.04
KOH (s)	2.35	0.03
NR latex	2.77	2.71
Iso-propanol	1.32	0.24
DI water	37.8	18.5
CHPO	2.49	3.29
TEPA	1.65	2.18
MMA	7.89 <sup>a</sup>	—

<sup>a</sup> Khan et al., Dielectric studies of MMA and BMA with primary alcohols using time domain reflectometry, *J. Pure & Appl. Phy.*, 2007, 45, 754-758.

Conditions: Frequency range = 1.6 – 2.6 GHz at 25°C

#### 4.2 Preliminary study of graft copolymerization induced by domestic microwave

From preliminary study, it was found that the graft copolymerization of MMA onto NR induced by microwave was possible. The initial data indicated that the microwave heating method is more effective comparatively than the conventional heating method. Table 4.2 shows the %grafting properties of graft product obtained from conventional method and domestic microwave method. Both %graft natural rubber (%GNR) and %grafting efficiency (%GE) obtained from domestic microwave at 100 W for 15 min (0.25 h) with 1.0 phr of initiator concentration and 50 phr of monomer concentration were higher than that from the conventional grafting method that spent longer reaction time (7 h). This is possible to explain that the microwave energy promote the higher contents of MMA and NR macroradicals which were the active sites for graft copolymerization (Singh et al., 2004).

**Table 4.2** Grafting properties of graft product obtained from conventional and domestic microwave methods

Grafting properties	Conventional method	Domestic microwave method
% Graft natural rubber (%GNR)	55.8	62.4
% Free NR	29.4	25.2
% Free PMMA	14.8	12.4
% Grafting efficiency (%GE)	45.1	59.7
Microwave power (W)	-	100
Time (h)	7	0.25
Reaction temperature (°C)	60	60

Conditions: [INT] = 1.0 phr, [MMA] = 50 phr

### 4.3 Graft copolymerization of MMA onto NR induced by adjustable microwave power

Due to the fluctuation of microwave power generated from the domestic microwave, the graft copolymerization of MMA onto NR was studied by using an adjustable microwave power apparatus. By comparing with the conventional grafting method at ca. 65% GNR, the graft copolymerization of MMA onto NR induced by microwave at 100 W required short reaction time (ca. 20 min) whereas the conventional method was carried out using longer reaction time as 7 h.

The effect of the reaction time on the grafting properties and %GE of graft product obtained from conventional method (CM) compared with microwave irradiation method is presented in Table 4.3. For the adjustable microwave method (MM), it could be seen that when the reaction time increased from 5-20 min, the %GNR and %GE increased from 50.3-65.2% and 52.0-58.2%, respectively. Above 20 min, the %GNR and %GE decreased slightly possibly due to decomposition of the GNR or NR macroradicals including MMA radicals (Sen and Pal, 2009). Furthermore, %free NR and %free PMMA obtained from the adjustable microwave method were lower than that from conventional method.

**Table 4.3** Grafting properties of graft product obtained from conventional method and adjustable microwave method at 60°C

Reaction time	%GNR		%Free NR		%Free PMMA		%GE	
	CM	MM	CM	MM	CM	MM	CM	MM
10 min	38.9 (1.0)*	50.3 (0.2)	48.2 (1.6)	37.7 (1.0)	13.0 (0.6)	12.0 (0.8)	52.0 (2.0)	52.0 (3.5)
20 min	44.1 (2.3)	65.2 (2.0)	44.0 (0.9)	23.2 (1.8)	11.9 (1.4)	11.6 (0.2)	54.9 (3.3)	58.2 (1.8)
30 min	47.0 (1.5)	63.2 (1.8)	41.2 (1.4)	23.1 (1.6)	11.7 (0.1)	13.8 (0.2)	57.2 (1.2)	55.2 (1.2)
40 min	58.7 (2.5)	59.1 (0.2)	31.5 (2.9)	29.0 (0.2)	9.8 (0.4)	11.9 (0.4)	61.3 (0.5)	53.3 (1.3)
60 min	59.3 (3.2)	53.9 (1.8)	31.1 (3.0)	33.3 (1.5)	9.5 (0.2)	12.8 (0.4)	63.4 (1.8)	49.2 (2.1)
7 h	67.4 (1.4)	-	24.0 (1.2)	-	8.6 (0.2)	-	68.3 (2.0)	-

\*The number in parenthesis is a standard deviation.

CM is a conventional method.

MM is an adjustable microwave method.

#### 4.4 Statistical analysis using 2<sup>4</sup> factorial design experiments for graft copolymerization

A factorial design experiment is carried out in this research in order to investigate the influence of studied parameters on the %grafting properties (%GNR, %free NR and %free PMMA) and %GE of graft product. The four main factors were initiator concentration (INT, A), monomer concentration (MMA, B), microwave power (MWP, C) and exposure time (ET, D). The results obtained from 2<sup>4</sup> factorial design experiment of graft copolymerization of MMA onto NR induced by microwave irradiation at 60°C are shown in Table 4.4. The design matrix and the average response data obtained from a two replicates of 2<sup>4</sup> factorial design experiments were shown in Table 4.5. The 32 runs were made in random order. The analysis of these data was started by constructing a normal probability plot of the effect estimates. The table of plus and minus signs for the calculation of contrast constants for the 2<sup>4</sup> factorial design are shown in Appendix F. From the obtained contrasts, the 15 factorial effects estimates and the sum of squares are shown in Appendix F.

**Table 4.4** Results from 2<sup>4</sup> factorial design experiment for graft copolymerization

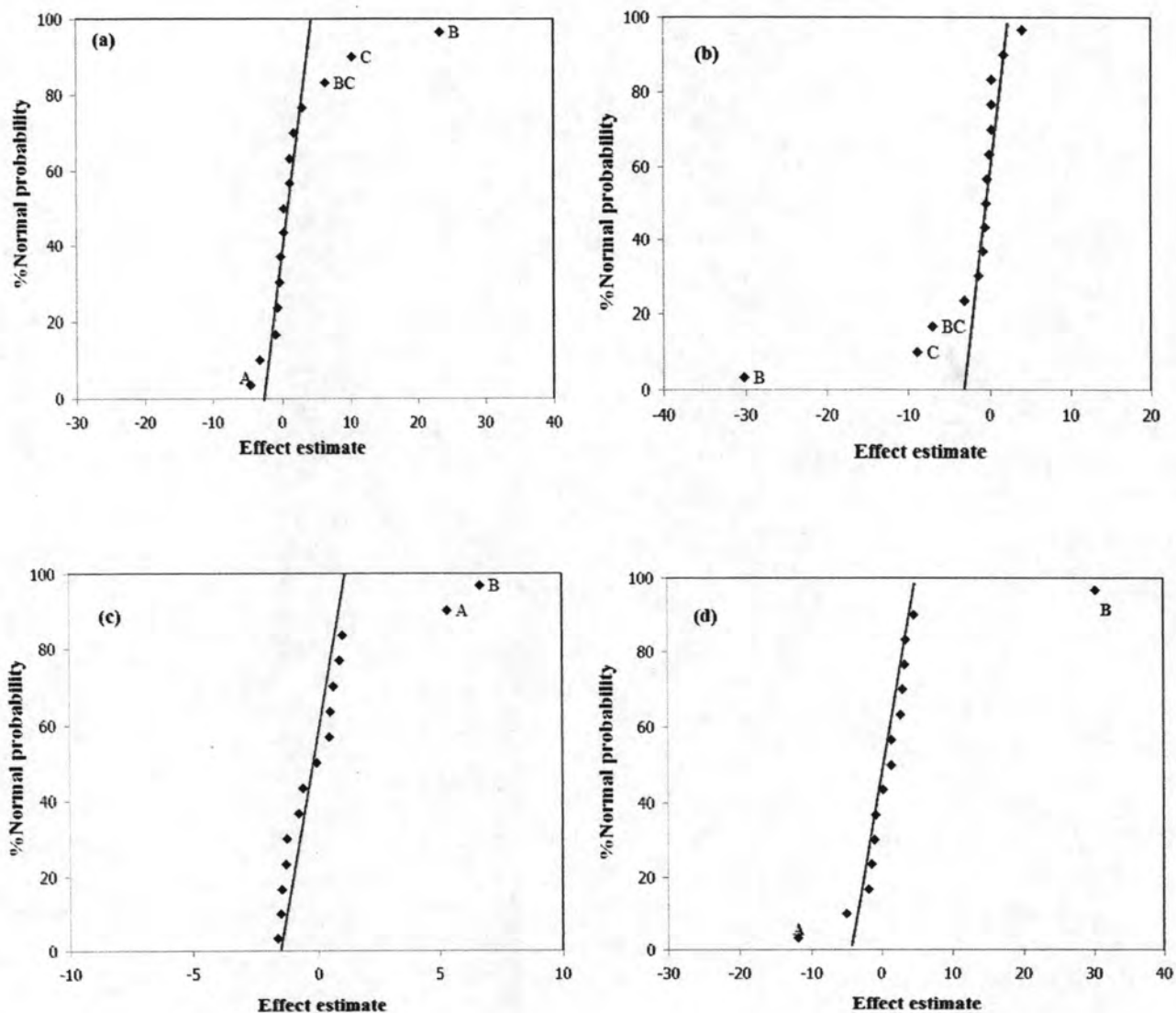
Exp.	Design factor				Graft	Free	Free	GE
	INT	MMA	MWP	ET	NR	NR	PMMA	
	(phr)	(phr)	(W)	(min)	(%)	(%)	(%)	(%)
GNR 01	0.5	25	50	10	36.7	58.0	5.3	38.0
GNR 02	0.5	25	50	10	37.8	56.1	6.1	40.5
GNR 03	2.5	25	50	10	33.2	54.8	12.0	14.9
GNR 04	2.5	25	50	10	33.6	56.3	10.1	18.8
GNR 05	0.5	75	50	10	57.2	29.1	13.7	57.0
GNR 06	0.5	75	50	10	56.1	30.6	13.3	52.9
GNR 07	2.5	75	50	10	45.0	35.8	19.2	54.2
GNR 08	2.5	75	50	10	43.3	37.8	18.8	53.4
GNR 09	0.5	25	150	10	41.2	53.7	5.1	33.9
GNR 10	0.5	25	150	10	38.3	56.5	5.2	32.9
GNR 11	2.5	25	150	10	39.1	54.4	6.4	14.7
GNR 12	2.5	25	150	10	37.0	57.0	6.0	15.8
GNR 13	0.5	75	150	10	66.7	23.5	9.9	69.6
GNR 14	0.5	75	150	10	64.4	25.1	10.5	65.7
GNR 15	2.5	75	150	10	70.0	12.5	17.4	48.7
GNR 16	2.5	75	150	10	67.3	15.9	16.8	47.4
GNR 17	0.5	25	50	30	35.7	59.6	4.8	29.4
GNR 18	0.5	25	50	30	33.4	62.2	4.4	27.3
GNR 19	2.5	25	50	30	33.9	56.1	10.0	22.2
GNR 20	2.5	25	50	30	34.7	53.2	12.1	19.3
GNR 21	0.5	75	50	30	58.2	34.8	7.0	70.1
GNR 22	0.5	75	50	30	55.1	37.4	7.4	65.6
GNR 23	2.5	75	50	30	51.8	30.1	18.1	53.4
GNR 24	2.5	75	50	30	48.3	35.3	16.4	56.8
GNR 25	0.5	25	150	30	45.3	50.9	3.7	41.7
GNR 26	0.5	25	150	30	42.3	53.8	3.9	37.2
GNR 27	2.5	25	150	30	35.3	56.6	8.1	25.1
GNR 28	2.5	25	150	30	32.1	58.5	9.3	31.3
GNR 29	0.5	75	150	30	74.9	14.1	11.0	61.6
GNR 30	0.5	75	150	30	70.7	17.6	11.7	55.6
GNR 31	2.5	75	150	30	68.3	18.0	13.7	59.6
GNR 32	2.5	75	150	30	66.5	19.2	14.3	55.9

**Table 4.5** Design matrix of  $2^4$  factorial design experiment for graft copolymerization of MMA onto NR at 60°C

Exp.	Run label	Design factor				Graft NR (%)	Free NR (%)	Free PMMA (%)	GE (%)
		INT	MMA	MWP	ET				
		A	B	C	D				
GNR 01	(1)	-	-	-	-	37.2 (0.7)*	57.1 (1.3)	5.7 (0.6)	39.3 (1.8)
GNR 02	<i>a</i>	+	-	-	-	33.4 (0.2)	55.5 (1.1)	11.1 (1.3)	16.8 (2.7)
GNR 03	<i>b</i>	-	+	-	-	56.6 (0.8)	29.9 (1.0)	13.5 (0.2)	55.0 (3.0)
GNR 04	<i>ab</i>	+	+	-	-	44.2 (1.2)	36.8 (1.5)	19.0 (0.3)	53.8 (0.6)
GNR 05	<i>c</i>	-	-	+	-	39.8 (2.1)	55.1 (1.9)	5.1 (0.1)	33.4 (0.7)
GNR 06	<i>ac</i>	+	-	+	-	38.1 (1.5)	55.7 (1.8)	6.2 (0.3)	15.3 (0.8)
GNR 07	<i>bc</i>	-	+	+	-	65.5 (1.6)	24.3 (1.2)	10.2 (0.5)	67.7 (2.7)
GNR 08	<i>abc</i>	+	+	+	-	68.7 (1.9)	14.2 (2.4)	17.1 (0.5)	48.0 (0.9)
GNR 09	<i>d</i>	-	-	-	+	34.5 (1.6)	60.9 (1.9)	4.6 (0.2)	28.4 (1.5)
GNR 10	<i>ad</i>	+	-	-	+	34.3 (0.6)	54.7 (2.1)	11.1 (1.5)	20.8 (2.1)
GNR 11	<i>bd</i>	-	+	-	+	56.7 (2.1)	36.1 (1.9)	7.2 (0.3)	67.8 (3.2)
GNR 12	<i>abd</i>	+	+	-	+	50.0 (2.5)	32.7 (3.7)	17.3 (1.2)	55.1 (2.5)
GNR 13	<i>cd</i>	-	-	+	+	43.8 (2.1)	52.4 (2.0)	3.8 (0.1)	39.5 (3.1)
GNR 14	<i>acd</i>	+	-	+	+	33.7 (2.3)	57.6 (1.4)	8.7 (0.9)	28.2 (4.3)
GNR 15	<i>bcd</i>	-	+	+	+	72.8 (3.0)	15.8 (2.5)	11.4 (0.5)	58.6 (4.3)
GNR 16	<i>abcd</i>	+	+	+	+	67.4 (1.3)	18.6 (0.8)	14.0 (0.5)	57.8 (2.6)

\*The number in parenthesis is a standard deviation.

The normal probability plots of these effects are shown in Figure 4.1. The effects following the line are negligible, whereas the important effects influencing the system far from the straight line. For the %GNR, the important effects are the effects of A, B, C and the BC interaction, whereas the effect of A is not important for the level of %free NR. For the %free PMMA and %GE, the values of these parameters are only depended on A and B.



**Figure 4.1** The normal probability plots of effect estimates on (a) %GNR (b) %free NR (c) %free PMMA and (d) %GE.

The analysis of variance (ANOVA) of %GNR, %free NR, %free PMMA and %GE is summarized in Table 4.6. The column labeled “Percent contribution” indicates the importance of each selected factors obtained from normal probability plots of the effects (Figure 4.1) to the total sum of square. The F test statistic is used to evaluate whether a factor has a significant effect ( $F_0 > F_{\alpha, v_1, v_2}$  where  $\alpha = 95\%$  confidence interval or 0.05;  $v_1 =$  degree of freedom for model and.  $v_2 =$  degree of freedom for insignificant factors or error). This F values for each model and factors are obtained from the table of percentage points of the F distribution



(Appendix Table IV in Montgomery, 2001). For example, the F value of %GNR model ( $F_{0.05,4,11}$ ) is 3.36 which is lower than  $F_0$  (71.03). Thus, it is concluded that the %GNR model is significant. This method is used to verify the significant of all models and selected factors as shown in Table 4.6.

Table 4.7 presents the results obtained from the calculation of effect estimate and coefficient estimate with their standard errors. It shows that the increase in the initiator concentration gave the negative effect for %GNR and %GE. It could be explained that the higher initiator concentration might promote the higher content of free radicals which had higher possibility to occur the recombination resulting to the reduction of %GNR and %GE. The similar observation was also indicated in the previous literature (Linda Thiraphattaraphun, 2001).

The increase in MMA concentration exhibited the positive effect for %GNR, %free PMMA and %GE whereas it was the negative effect for %free NR. Because the %GNR, %free PMMA and %GE increased with increasing amount of MMA. It could be explained that the higher monomer content promoted PMMA-homopolymerization and graft copolymerization with lower %free NR. However, the homopolymerization might compete with the grafting reaction at higher monomer concentrations. Another explanation, the newly arriving monomers are sterically hindered, resulting in limiting grafting at higher monomer concentrations (Suriyachi et al., 2004).

The microwave power showed the positive effect on %GNR but no effect on %free PMMA and %GE. However, it was the negative effect for %free NR. This was possible that the microwave power might promote the greater contents of MMA monomer and NR macroradicals which were the active grafting sites for graft copolymerization (Tiwari and Singh, 2008). From the above reason, the %GNR increase with increasing the microwave power, whereas %free NR decrease with reduction the microwave power, simultaneously.

Furthermore, the experimental results indicated that %GNR, %free NR, %free PMMA and %GE were not depended on the exposure time over the range of study.

**Table 4.6** Analysis of variance for  $2^4$  factorial design experiment

Model term	Sum of squares	Percent contribution	Degree of freedom	Mean square	$F_0$	$F_{\alpha, v_1, v_2}$ (from table)
<b>1) %GNR</b>						$F_{0.05, 4, 11}$
Model	2863.51	96.27	4	715.88	71.03	3.36
A	86.34	2.90	1	86.34	8.57	4.84
B	2186.49	73.51	1	2186.49	216.94	4.84
C	428.58	14.41	1	428.58	42.52	4.84
BC	162.11	5.45	1	162.11	16.08	4.84
Error	110.87	3.73	11	10.08		
Total	2974.37		15			
<b>2) %Free NR</b>						$F_{0.05, 3, 12}$
Model	4110.18	97.03	3	1370.06	130.56	3.49
B	3614.54	85.33	1	3614.54	344.46	4.75
C	305.21	7.20	1	305.21	29.09	4.75
BC	190.43	4.50	1	190.43	18.15	4.75
Error	125.92	2.97	12	10.49		
Total	4236.10		15			
<b>3) %Free PMMA</b>						$F_{0.05, 1, 13}$
Model	293.35	84.13	2	146.68	34.47	3.81
A	114.83	32.93	1	114.83	26.99	4.67
B	178.52	51.20	1	178.52	41.95	4.67
Error	55.32	15.87	13	4.26		
Total	348.67		15			
<b>4) %GE</b>						$F_{0.05, 2, 13}$
Model	4215.80	91.30	2	2107.90	68.20	3.81
A	551.38	11.94	1	551.38	17.84	4.67
B	3664.42	79.36	1	3664.42	118.56	4.67
Error	401.78	8.70	13	30.91		
Total	4617.59		15			

**Table 4.7** Calculation of effect estimate, coefficient estimate and standard error of 2<sup>4</sup> factorial design experiment for graft copolymerization

Effect name	Effect estimate	± Standard error	Coefficient estimate	± Standard error
<b>1) Average %GNR</b>			48.5	± 0.79
<b>Main effects</b>				
Initiator concentration, INT	-4.65	± 1.58	-2.32	± 0.79
Monomer concentration, MMA	23.4	± 1.58	11.7	± 0.79
Microwave power, MWP	10.4	± 1.58	5.18	± 0.79
<b>Two-factor interaction</b>				
MMA*MWP	6.37	± 1.58	3.18	± 0.79
<b>2) Average %free NR</b>			41.1	± 0.81
<b>Main effects</b>				
Monomer concentration, MMA	-30.1	± 1.62	-15.0	± 0.81
Microwave power, MWP	-8.74	± 1.62	-4.37	± 0.81
<b>Two-factor interaction</b>				
MMA*MWP	-6.90	± 1.62	-3.45	± 0.81
<b>3) Average %free PMMA</b>			10.4	± 0.52
<b>Main effects</b>				
Initiator concentration, INT	5.36	± 1.04	2.68	± 0.52
Monomer concentration, MMA	6.68	± 1.04	3.34	± 0.52
<b>4) Average %GE</b>			42.8	± 1.39
<b>Main effects</b>				
Initiator concentration, INT	-11.7	± 2.78	-5.87	± 1.39
Monomer concentration, MMA	30.3	± 2.78	15.1	± 1.39

#### 4.4.1 Regression model

From the analysis of variance of four response models for graft copolymerization of MMA onto NR, the coefficient estimate of each response model was obtained for the regression mode. In a  $2^4$  factorial design experiment, it is easy to express the results of the experiment in terms of a regression model. In this research, the regression model for predicting %GNR, %free NR, %free PMMA and %GE as shown in Eq. 4.1 - 4.4.

$$\hat{Y}_1 = 48.54 - 2.32X_1 + 11.69X_2 + 5.18X_3 + 3.18 X_2 X_3 \quad (4.1)$$

$$\hat{Y}_2 = 41.09 - 15.03X_2 - 4.37 X_3 - 3.45 X_2 X_3 \quad (4.2)$$

$$\hat{Y}_3 = 10.37 + 2.68X_1 + 3.34X_2 \quad (4.3)$$

$$\hat{Y}_4 = 42.83 - 5.87X_1 + 15.13X_2 \quad (4.4)$$

where  $\hat{Y}_1$ ,  $\hat{Y}_2$ ,  $\hat{Y}_3$  and  $\hat{Y}_4$  are the predicted values or fitted value of %GNR, %free NR, %free PMMA and %GE, respectively.  $X_1$ ,  $X_2$  and  $X_3$  are coded factor for initiator concentration (INT), monomer concentration (MMA) and microwave power (MWP).

This regression model can be used to obtain the predicted or fitted value ( $\hat{Y}$ ) in 16 experiments of  $2^4$  factorial design for graft copolymerization of MMA onto NR induced by microwave irradiation.

#### 4.4.2 Residuals and model adequacy checking

Before applying the regression model for  $2^4$  factorial design experiment for graft copolymerization. The residuals of  $2^4$  factorial design should be checked to confirm whether the model is correct and adequate.

For example, the analysis of variance (ANOVA) for %GNR model indicates that the only significant effects are  $A = -2.32$ ,  $B = 11.69$ ,  $C = 5.18$  and  $BC = 3.18$ . If this model is true, the estimated %GNR is given by Eq. 4.1.

According to the definition, the residuals ( $e$ ) are the differences between the observed values ( $Y$ ) and predicted values ( $\hat{Y}$ ). For example (GNR01 entry), all factors ( $A$ ,  $B$  and  $C$ ) were at low level ( $-1$ ). Thus, the predicted values of %GNR was calculated from Eq.4.5.

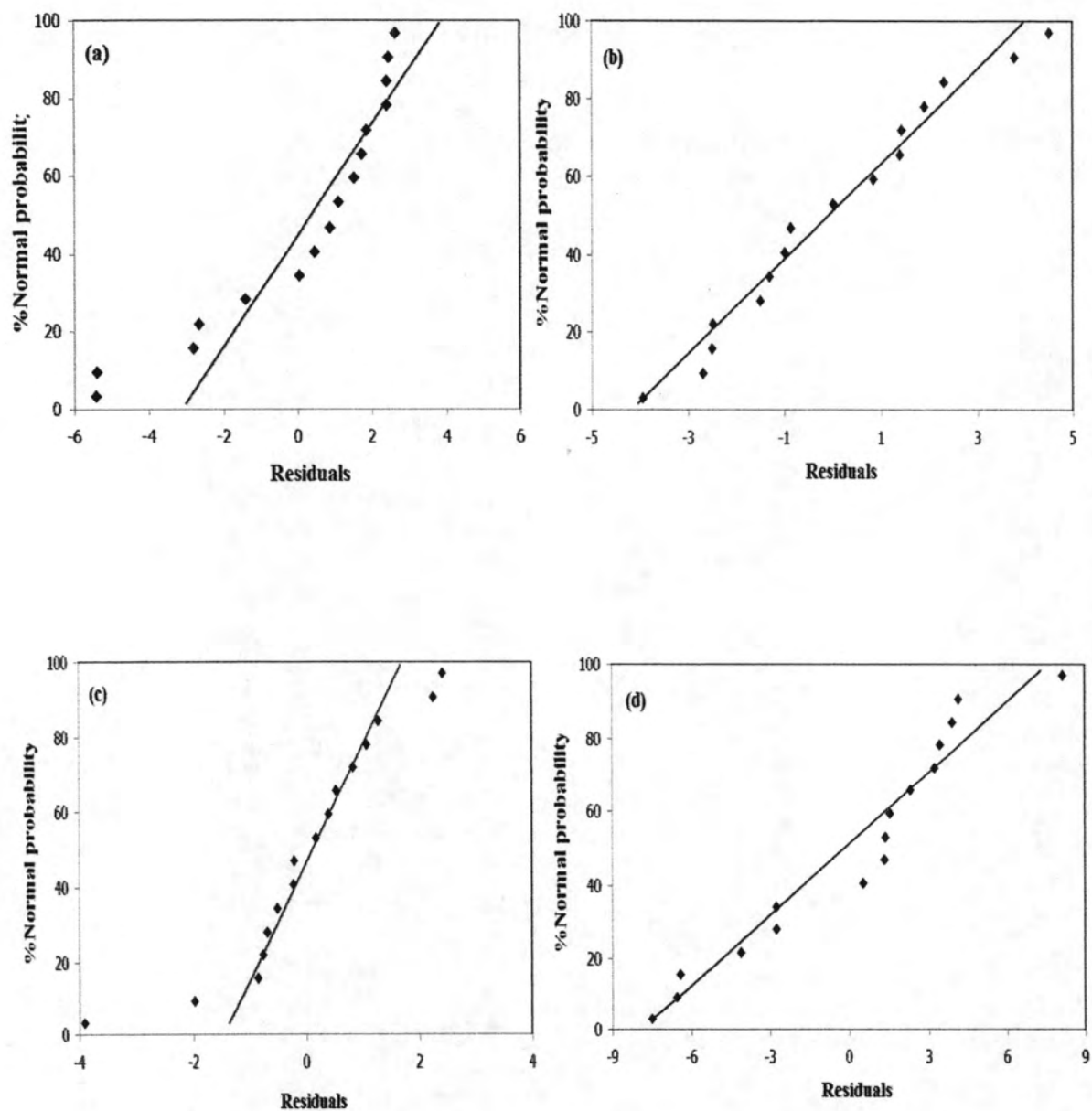
$$\begin{aligned}\hat{Y} &= 48.54 - 2.32(-1) + 11.69(-1) + 5.18(-1) + 3.18(-1)(-1) \quad (4.5) \\ &= 37.17\end{aligned}$$

Because the observed %GNR ( $Y$ ) is 37.22, the residual  $e$  is 0.05. The observed values, predicted values and residuals for all 16 observations of %GNR, %free NR, %free PMMA and %GE are shown in Table 4.8.

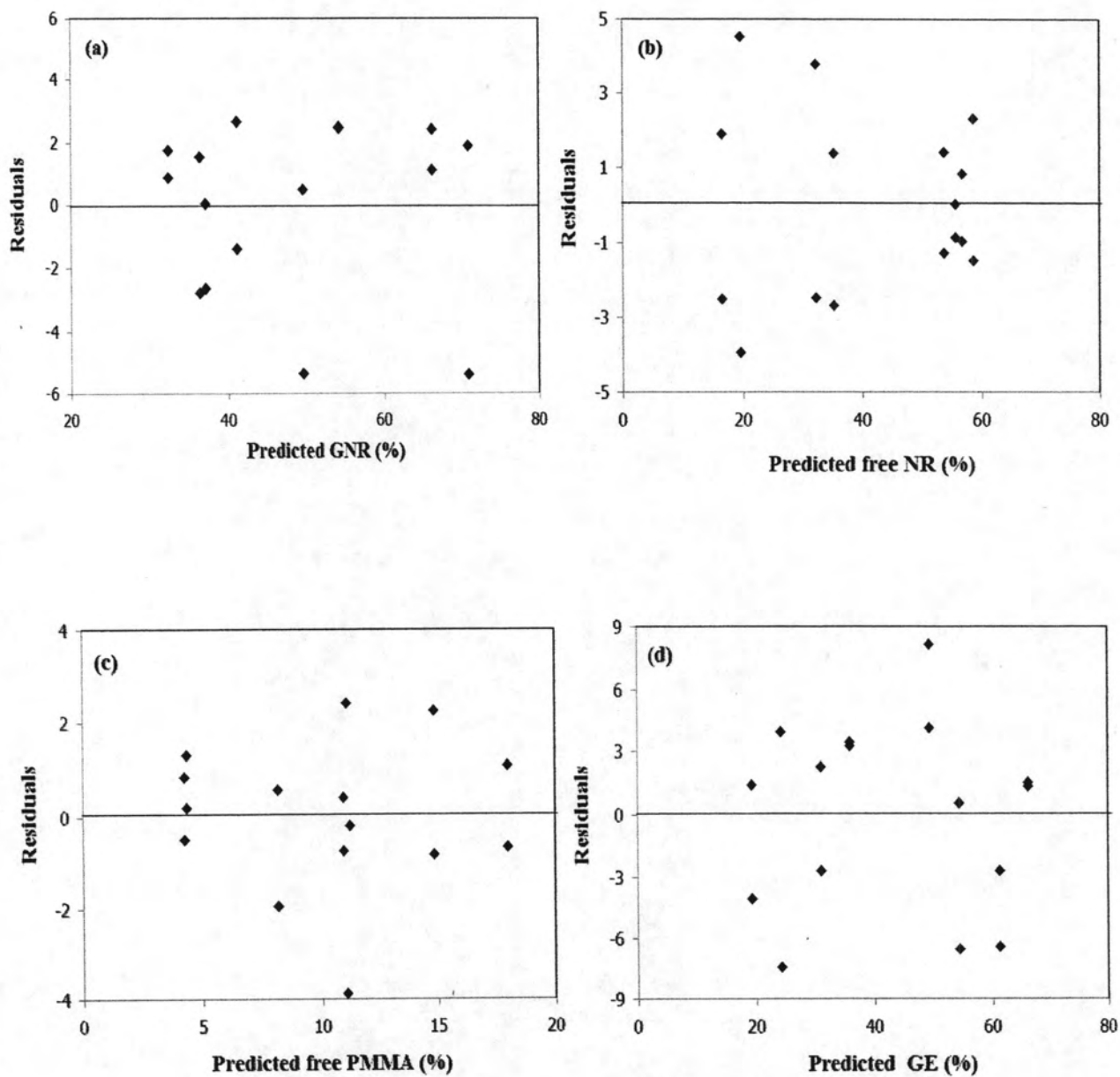
The normal probability plots of the residuals of %GNR, %free NR, %free PMMA and %GE are shown in Figure 4.2. The points on these plots lie reasonably close to a straight line. For example, this result supports the conclusion that  $A$ ,  $B$ ,  $C$  and  $BC$  are the only significant effects on %GNR from the ANOVA results. Furthermore, the %GNR model is also checked the correct of the model by the plot of the residuals versus the predicted %GNR. The plots of the residuals versus the predicted values of %GNR, %free NR, %free PMMA and %GE are shown in Figure 4.3. These plots are now satisfactory due to not appear obvious pattern or structureless. It can be concluded that the %GNR model for graft copolymerization requires only factor  $A$ ,  $B$ ,  $C$  and  $BC$  for adequate interpretation. The method for this analysis was applied for all model of responses.

**Table 4.8** The observed value, predicted value and residuals of %GNR, %free NR, %free PMMA and %GE

Entry	Run label	%GNR			%Free NR			%Free PMMA			%GE		
		Observed value	Predicted value	Residuals	Observed value	Predicted value	Residuals	Observed value	Predicted value	Residuals	Observed value	Predicted value	Residuals
GNR 01	(1)	37.22	37.17	0.05	57.07	58.55	-1.48	5.71	4.42	1.29	39.28	36.03	3.25
GNR 02	a	33.41	32.54	0.88	55.53	55.51	0.02	11.05	11.27	-0.21	16.81	24.29	-7.48
GNR 03	b	56.62	54.20	2.43	29.87	32.35	-2.48	13.51	11.10	2.41	54.95	61.37	-6.42
GNR 04	ab	44.18	49.55	-5.37	36.79	35.39	1.40	19.03	17.95	1.08	53.77	49.63	4.14
GNR 05	c	39.76	41.17	-1.41	55.11	53.68	1.43	5.14	4.29	0.84	33.42	31.10	2.31
GNR 06	ac	38.06	36.52	1.54	55.74	56.72	-0.98	6.20	8.16	-1.96	15.27	19.36	-4.09
GNR 07	bc	65.51	70.91	-5.40	24.27	19.76	4.52	10.22	10.97	-0.75	67.65	66.30	1.36
GNR 08	abc	68.68	66.27	2.41	14.22	16.72	-2.49	17.10	14.84	2.26	48.01	54.56	-6.55
GNR 09	d	34.53	37.18	-2.66	60.87	58.55	2.32	4.61	4.42	0.19	28.37	31.10	-2.73
GNR 10	ad	34.27	32.54	1.74	54.66	55.51	-0.85	11.07	11.27	-0.20	20.76	19.36	1.39
GNR 11	bd	56.66	54.20	2.47	36.13	32.35	3.78	7.21	11.10	-3.89	67.84	66.30	1.54
GNR 12	abd	50.03	49.55	0.48	32.70	35.39	-2.69	17.27	17.95	-0.67	55.08	54.56	0.53
GNR 13	cd	43.83	41.17	2.66	52.38	53.68	-1.30	3.79	4.29	-0.50	39.46	36.03	3.43
GNR 14	acd	33.73	36.52	-2.79	57.57	56.72	0.85	8.71	8.16	0.55	28.21	24.29	3.92
GNR 15	bcd	72.79	70.91	1.87	15.83	19.76	-3.93	11.38	10.97	0.41	58.63	61.37	-2.74
GNR 16	abcd	67.38	66.27	1.12	18.62	16.72	1.90	14.00	14.84	-0.84	57.78	49.63	8.14



**Figure 4.2** The normal probability plots of the residuals of (a) %GNR (b) %free NR (c) %free PMMA and (d) %GE.



**Figure 4.3** The plots of the residuals versus the predicted values of (a) %GNR (b) %free NR (c) %free PMMA and (d) %GE.

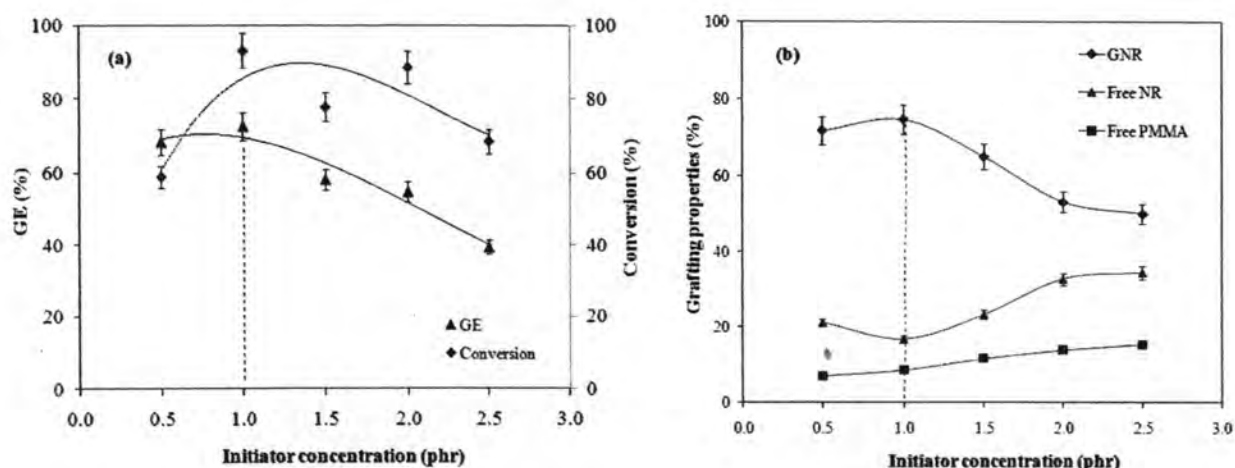


## 4.5 Univariate experiments for graft copolymerization

The statistical experiments described above provide only information on the significance of the factors. In order to determine how each factor affects the %grafting properties (%GNR, %free NR, %free PMMA) and %GE, the univariate experiments of the central composite design of the parameters were carried out individually as shown in Figure 4.4 - 4.7. The central condition applied for the univariate experiments were 1.5 phr and 50 phr of initiator and monomer concentrations, respectively under 100 W of microwave power at 60°C for 20 min. The raw data are presented in Table D-7 in Appendix D.

### 4.5.1 Effect of initiator concentration

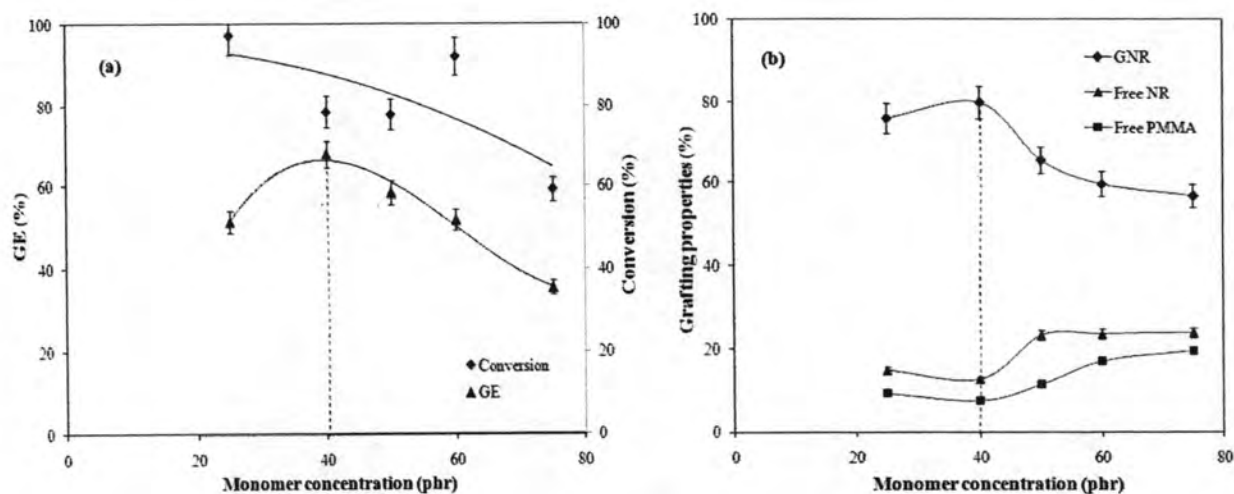
The effects of initiator concentration on the %grafting properties including %conversion and %GE of graft product are shown in Figure 4.4. The range of initiator concentration was varied between 0.5 to 2.5 phr. The monomer concentration was kept constant at 50 phr under 100 W of microwave power at 60°C for 20 min. The results indicated that the %GE (Figure 4.4a) and %GNR (Figure 4.4b) slightly increase with increasing initiator concentration in the range 0.5-1.0 phr due to the higher grafting sites. When initiator concentration was above 1.0 phr, %GNR, %GE and %conversion tended to decrease. It is possible to explain that the higher initiator concentration produced the higher content of free radicals. This had high possibility to cause the termination via recombination of these free radicals. Furthermore, it was also found that the %free NR and the %free PMMA slightly increased with increasing initiator concentration. It could be explained that the higher initiator concentration also promoted the occurrence of the higher homopolymer PMMA in the system (Suriyachi et al., 2004).



**Figure 4.4** Effect of initiator concentration on (a) %conversion and %GE and (b) %grafting properties ([MMA] = 50 phr, microwave power = 100 W, exposure time = 20 min at 60°C).

#### 4.5.2 Effect of monomer concentration

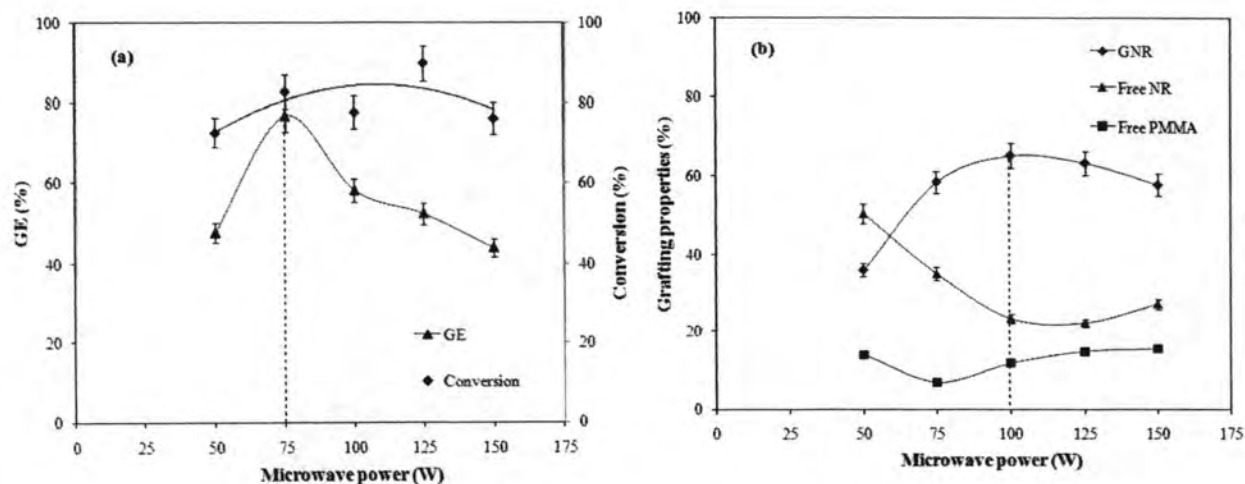
Figure 4.5 shows the effect of monomer concentration on the %grafting properties, %GE and %conversion of graft product obtained from graft copolymerization induced by microwave energy at 100 W for 20 min at 60°C. As the monomer concentration increases in the range of 20-40 phr, %GE (Figure 4.5a) and %GNR (Figure 4.5b) slightly increase and then decrease when the monomer content was higher than 40 phr. This result might be explained by a mechanism involving a surface-controlled process. This suggested that the graft copolymerization mainly occurred on the surface of NR latex particles. When grafting proceeds and a certain shell thickness of the second-stage polymer was reached, the contact area between MMA monomer and NR would be decreased due to difficulty of MMA diffusion to react with grafting sites on the NR structure (Wanvimon Arayapranee et al., 2002). Thus, the homopolymer (PMMA) content tended to increase with increasing the MMA concentration in the system. For %conversion (Figure 4.5a), the overloading of MMA content might cause the decomposition or volatilization under microwave irradiation resulting to the loss of monomer leading to the reduction of %conversion. The results were similar to the observation for microwave assisted radical grafting of maleic anhydride onto polyethylene (Wang et al., 2003).



**Figure 4.5** Effect of monomer concentration on (a) %conversion and %GE and (b) %grafting properties ( $[INT] = 1.5$  phr, microwave power = 100 W, exposure time = 20 min at 60°C).

#### 4.5.3 Effect of microwave power

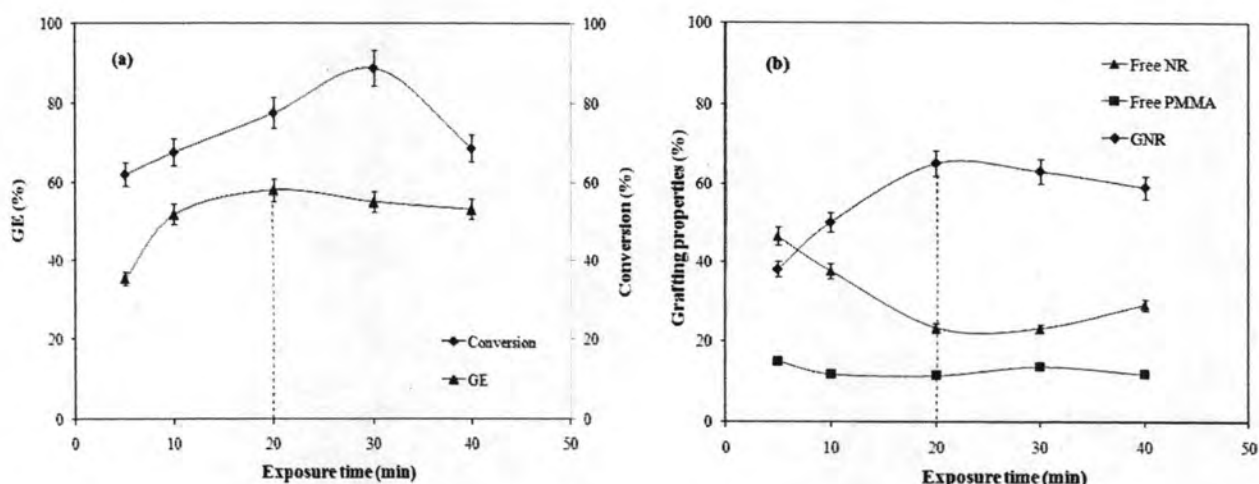
To study the effect of microwave power on the %grafting properties, %GE and %conversion of graft product, the microwave power was varied from 50 to 150 W as shown in Figure 4.6. It indicates that the increase in the microwave power in the range of 50-100 W increased %GNR and %conversion with decreasing %free NR and %free PMMA. This might be due to the formation of higher MMA radicals and NR macroradicals that were ready for graft copolymerization (Singh et al., 2006). However, the microwave power higher than 100 W promoted the formation of homopolymer or decomposition of the graft product (Singh et al., 2006) resulting to the reduction of %GE (Figure 4.6a) and %GNR (Figure 4.6b).



**Figure 4.6** Effect of microwave power on (a) %conversion and %GE and (b) %grafting properties ([INT] = 1.5 phr, [MMA] = 50 phr, exposure time = 20 min at 60°C).

#### 4.5.4 Effect of exposure time

Figure 4.7 shows the effect of exposure time on the %grafting properties, %GE and %conversion of graft product obtained from the microwave induced graft copolymerization of MMA onto NR at 100 W and at 60°C. The increase in the exposure time from 5 to 20 min increased %GE, %conversion (Figure 4.7a) and %GNR (Figure 4.7b). It could be explained that more microwave energy was absorbed resulting to the formation of higher MMA radicals and NR macroradicals including initiator radicals. This result was similar to the observation for microwave accelerated grafting of poly(acrylamide) onto starch (Singh et al., 2006). When exposure time was longer than 20 min, the %GNR and %GE tended to slightly decrease. This result is possibly related to the competition of graft copolymerization and partial degradation of monomer or initiator radicals. Moreover, the decomposition or volatilization of MMA at long exposure time is significant. Therefore, there is only a few MMA available to be used for graft copolymerization (Wang et al., 2003).



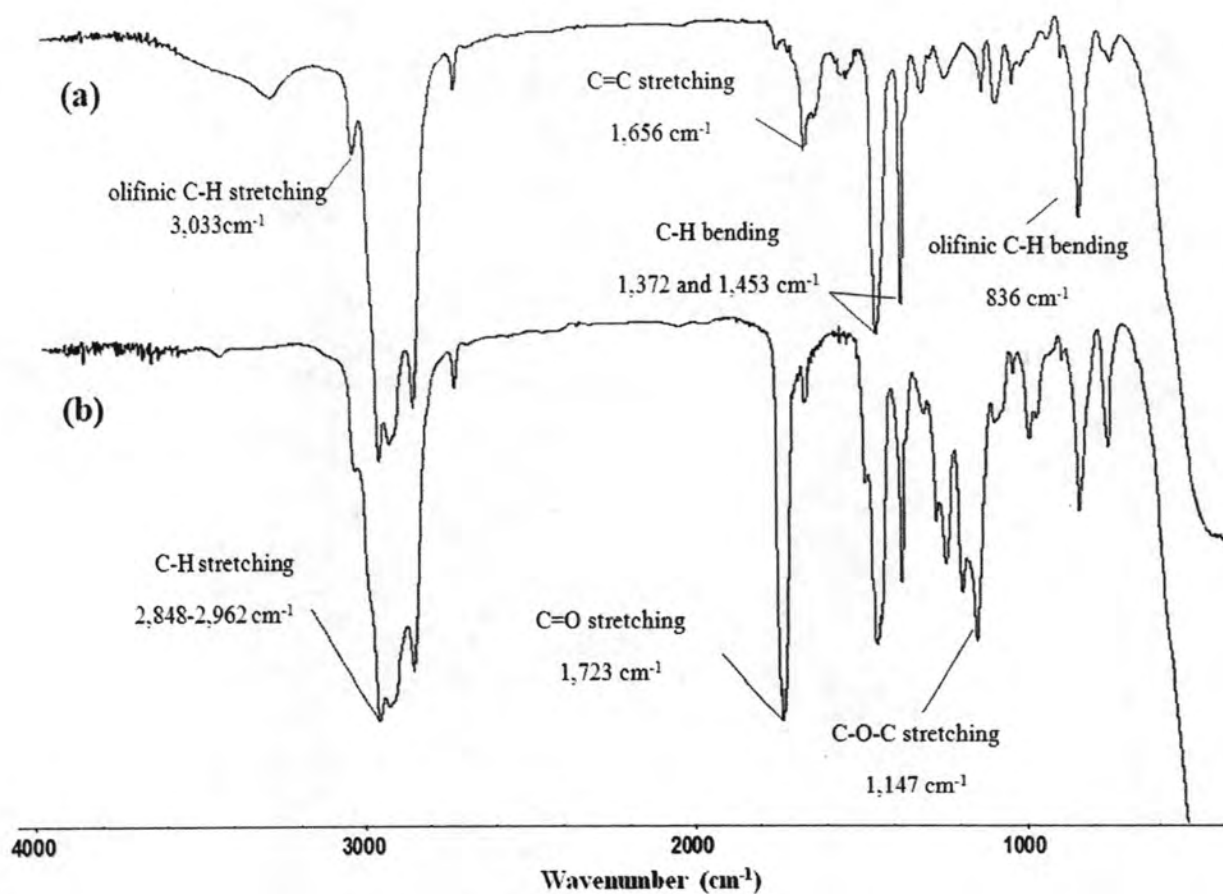
**Figure 4.7** Effect of exposure time on (a) %conversion and %GE and (b) %grafting properties ([INT] = 1.5 phr, [MMA] = 50 phr, microwave power = 100 W at 60°C).

#### 4.6 Structure characterization of GNR

The graft product obtained from microwave induced graft copolymerization of MMA onto NR with 1.5 phr and 50 phr of initiator and MMA under 100 W of microwave power for 20 min is shown in Figure 4.8. The structure of graft product obtained after soxhlet extraction (GNR) was analyzed by using FTIR and  $^1\text{H-NMR}$  spectroscopy. The FTIR spectra of NR and GNR are shown in Figure 4.9. The FTIR spectra of NR structure (Figure 4.9a) exhibited the characteristic absorption bands of olefinic C-H stretching vibration at  $3,033\text{ cm}^{-1}$ , aliphatic C-H stretching vibration at  $2,848\text{-}2,962\text{ cm}^{-1}$ , C=C stretching vibration at  $1,656\text{ cm}^{-1}$ , C-H bending vibration at  $1,372$  and  $1,453\text{ cm}^{-1}$  and olefinic C-H bending at  $836\text{ cm}^{-1}$ . The new peaks in FTIR spectrum of the GNR (Figure 4.13b) showed the characteristic absorption bands of C=O stretching at  $1,723\text{ cm}^{-1}$  and the C-O-C stretching at  $1,147\text{ cm}^{-1}$ . This result confirms that MMA was grafted onto NR backbone.

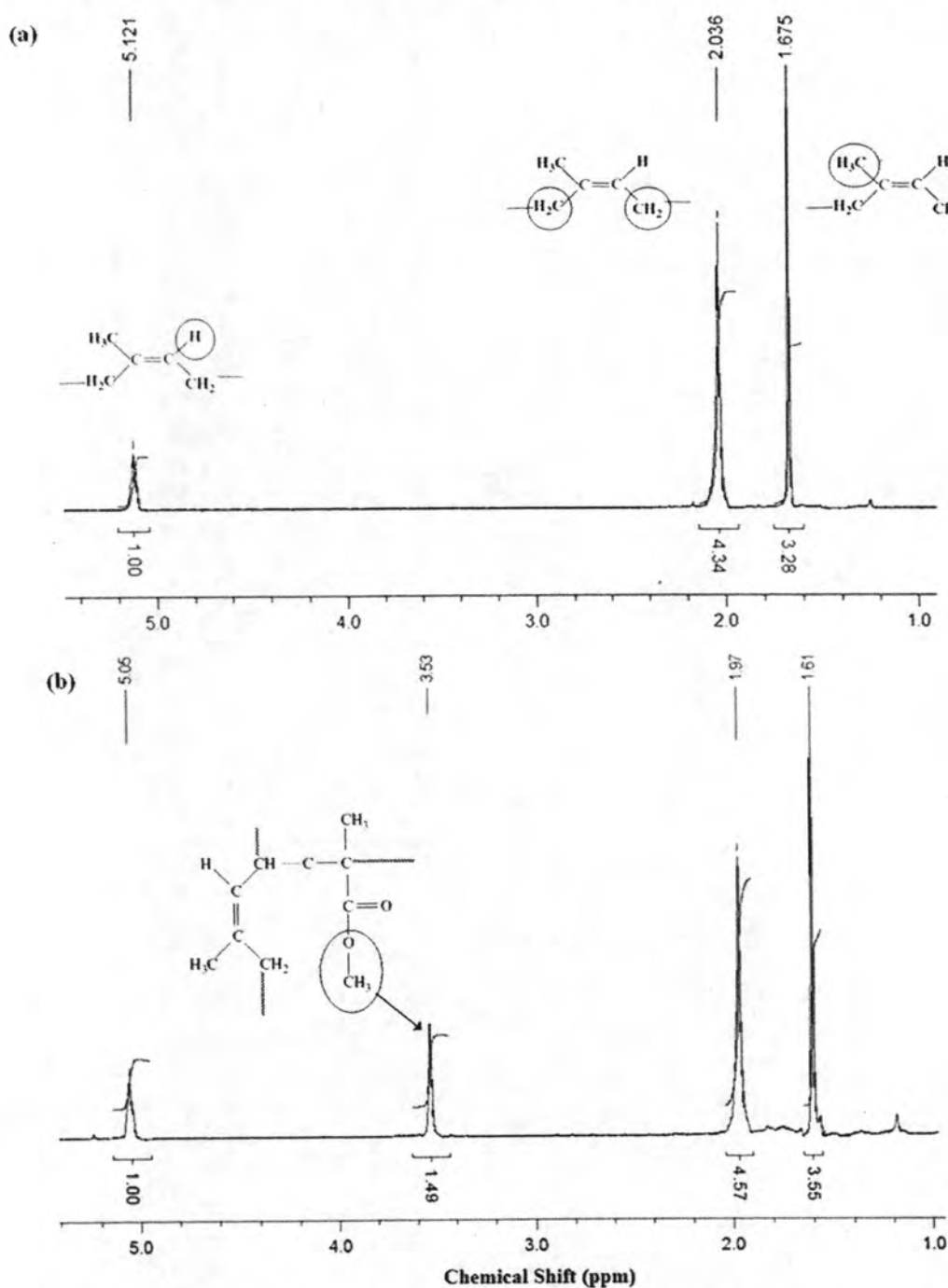


**Figure 4.8** Gross graft product obtained from microwave induced graft copolymerization of MMA onto NR at 100 W for 20 min (%GNR = 65.2).



**Figure 4.9** FTIR spectra of (a) NR and (b) GNR obtained from microwave induced graft copolymerization of MMA onto NR (%GNR = 65.2).

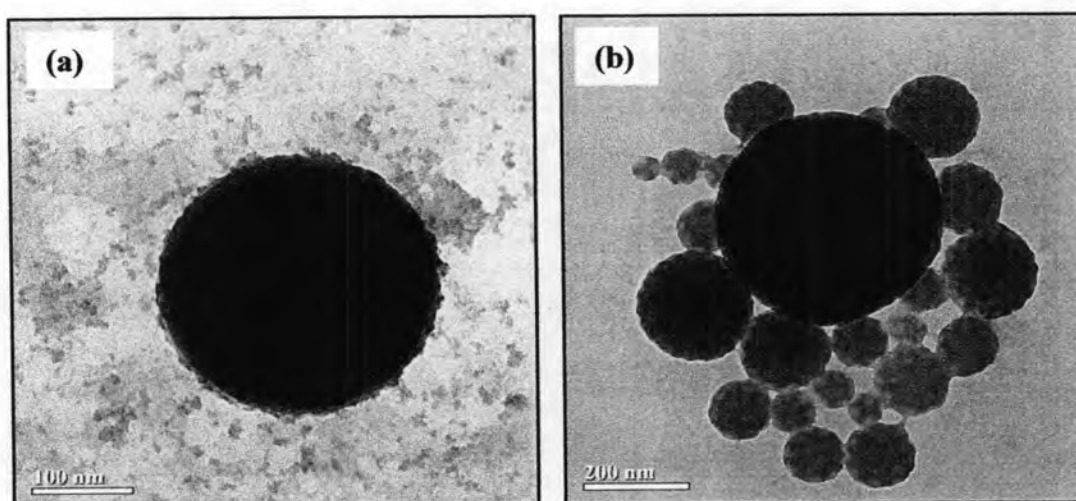
Figure 4.10 shows a comparison of NR and GNR structures evaluated by using  $^1\text{H-NMR}$  spectroscopy. Figure 4.10a presents the  $^1\text{H-NMR}$  spectrum of NR. The olefinic proton ( $\text{C}=\text{C}-\text{H}$ ) shows a singlet resonance signal at 5.12 ppm. The signal at 2.04 and 1.68 ppm attributed to the methylene proton ( $-\text{CH}_2$ ) and methyl proton ( $-\text{CH}_3$ ), respectively. After graft copolymerization, the new signal of methoxy proton ( $-\text{OCH}_3$ ) of the acrylic group in the GNR structure appeared at 3.53 ppm (Figure 4.10b). This result confirms the occurrence of grafting of MMA onto NR.



**Figure 4.10**  $^1\text{H-NMR}$  spectra of (a) NR and (b) GNR obtained from microwave induced graft copolymerization of MMA onto NR (%GNR = 65.2).

#### 4.7 Morphology of GNR

Graft copolymerization is a surface-controlled process because the bipolar redox initiator, coupled CHPO/TEPA, favors the particle/water interface as the locus of polymerization. The graft reaction of MMA onto NR is a core-shell type, emulsion polymerization. The GNR particles consist of the NR core and the compatibilized PMMA shell. During the course of polymerization, old polymer molecules would be encapsulated with new polymer molecules in the postulated encapsulation mechanism. The graft product latex obtained from the microwave induced graft copolymerization of MMA onto NR with 1.5 phr of initiator and 50 phr of MMA at 75 W for 20 min (76.8 %GE) was analyzed by using transmission electron microscopy (TEM) as shown in Figure 4.11. The darker areas represent the NR core regions, while the lighter areas are PMMA films as shells. The presence of nodules on the surfaces of the graft product particles might be due to the growing macroradical chains, which were grafted onto the surface of NR particles and continued to propagate to form the shell layer (Wanvimon Arayapranee et al., 2002).



**Figure 4.11** TEM micrographs of the particle morphologies of a) NR and b) GNR (%GE = 76.8).