

## PREPARATION AND CHARACTERIZATION OF STYRENE-METHYL METHACRYLATE IN DEPROTEINIZED NATURAL RUBBER LATEX (SMMA-DPNR)

*Siti Hajjar Che Man,<sup>1,2</sup> Azanam S. Hashim,<sup>1</sup> Hazizan Md. Akil<sup>1</sup>*

<sup>1</sup> *School of Material and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, Nibong Tebal, 14300 Pulau Pinang*

<sup>2</sup> *Department of Polymer Engineering, Universiti Teknologi Malaysia, Skudai, Johor*

### ABSTRACT

The graft polymerization of Styrene and Methyl Methacrylate (MMA) onto deproteinized natural rubber latex (SMMA-DPNR) was carried out using ammonium peroxy disulfate ( $N_2H_8O_8S_2$ ) as an initiator. The suitable reaction conditions based on the higher monomer conversion was determined. The SMMA-DPNR at 6 hours reaction time was successfully prepared with degree of conversion more than 99 %. The copolymers composition of the resultant SMMA-DPNR was obtained using <sup>1</sup>H-NMR Spectroscopy. As expected, composition of styrene in DPNR was higher than that of MMA due to the higher reactivity ratio of styrene monomer as compared to MMA monomer and the structure of the NR backbone.

#### **Keywords:**

Deproteinized Natural Rubber Latex, Styrene, Methyl Methacrylate, copolymer, <sup>1</sup>H NMR

### INTRODUCTION

Despite the increasingly research on synthetic rubber, natural rubber is still remain as a practically irreplaceable elastomer. It is an unsaturated elastomer with excellent physical properties includes high resilience, high strength, high elongation at breaks and good fatigue resistance. The fact that it is a renewable resource together with the good properties means that it is a very important elastomeric material. Especially with the current increasing awareness of environmental issues which has created a high level of interest in NR and its derivatives as compared to its synthetic counterparts which are mostly manufactured from non-renewable oil-based resources. The current oil crisis issue also gives significant credit to the increase in research on NR.

However, NR is quite sensitive to heat and oxidation due to the presence of the double bond on its chains. These inherent drawbacks of NR have limited its application in industry. In efforts to extend its use, various methods developed in order to modify its properties, through physical and chemical modifications [1].

On chemical modification, the grafting of vinyl monomers onto NR especially styrene and MMA monomers have been extensively studied [2-9]. Improved properties of the modified NR have led to many technical applications. It was also reported that graft copolymers can be used effectively as compatibilizer for polymer blends [10]. Recently a number of studies on the polymerizations of styrene or MMA using DPNR were reportedly increased, partly due to the allergy issue associated with natural rubber latex caused by the presence of protein [11, 12]. The allergy caused by natural rubber latex products has become a serious problem and therefore, DPNR is an obvious choice in the application where allergy is to be avoided. Furthermore, recent report has found that the grafting efficiency was higher when polymerizing MMA in DPNR latex as compared to NR latex [11]. The difference

was attributed to the removal of proteins which acted as free radical scavengers which terminated the free-radical species during the graft polymerization.

In this work, styrene and MMA monomers were grafted onto DPNR latex using emulsion polymerization technique. It is the intention of this study to have the monomers polymerization occur in the rubber particles to impart high degree of grafting by targeting the reaction directly onto rubber particles, so that no surfactant was added into the polymerization system [13]. Consequently, the reaction parameters were determined and the compositions of SMMA-DP NR copolymer were studied using  $^1\text{H}$  NMR.

## EXPERIMENTAL

### **Materials**

The DP NR latex used was supplied by Sumirubber Industries (Malaysia) Sdn. Bhd. The DRC of DP NR latex was 59 wt % with nitrogen content of 0.047 wt %. The low amount of nitrogen indicates that the latex is highly deprotenized. The latex also contains 0.65 g / l  $\text{H}_2\text{O}$  of sodium dodecyl sulfate which was added during deproteinization process. All the chemicals used in this experiment were of standard laboratory grade. Styrene monomer (FLUKA, purity ~ 99 %) was prepared free of an inhibitor by washing with a 10% sodium hydroxide solution followed by distilled water. The MMA monomer (FLUKA, purity ~ 99 %) was purified using rotary evaporator which is operated under vacuum condition. Both the styrene and MMA monomers were kept in a refrigerator prior to use. The initiator, Ammonium peroxy disulfate ( $\text{N}_2\text{H}_8\text{O}_8\text{S}_2$ ) was also purchased from Fluka Chemical Company. Deionised and distilled water were used throughout the work.

### **Polymerization**

The graft polymerization of styrene and MMA in DP NR latex was carried out in a 1 liter reaction vessel. The latex and water were first charged into the reactor and the dissolved oxygen present in the mixture was removed by purging nitrogen gas under continuous stirring for 15 minutes. The mixture of styrene and MMA monomer were fed to the reactor dropwise until the addition complete. When the desired temperature inside the reactor is achieved, the initiator solution was quickly added and the reaction temperature is recorded immediately after the addition of initiator completed. During the polymerization, samples of the polymerized latex were taken at certain time intervals for the determination of degree of conversion. The degree of conversion of monomer to polymer was determined gravimetrically and calculated as equation (1).

$$\text{Conversion (\%)} = \frac{(A - B)}{A} \times 100 \quad (1)$$

Where:

- A: Mass of monomer used for polymerization reaction (g)
- B: Mass of non-reacted monomer (g)

The polymerized latex were then sheeted by casting the latex on glass trays and dried overnight at room temperature. Once dried, the sheets were removed from the glass tray. The post treatments included the leaching process for 24 hours with 3 times of water changing and drying to the constant weight under vacuum at  $50^\circ\text{C}$ . The leaching process is to remove any water-soluble impurities from the rubber [3].

### **<sup>1</sup>H NMR Analysis**

The copolymer reaction efficiency has been evaluated by <sup>1</sup>H NMR. The samples of DPNR and SMMA-DPNR were swollen for 12 hours in deuterated chloroform and analyzed by <sup>1</sup>H NMR in a 400 MHz spectrometer ( Bruker) at 20 °C.

## **RESULT AND DISCUSSION**

### ***Polymerization of styrene-MMA in DPNR latex***

Summary of the recipes, reaction conditions and conversions efficiency is outlined in Table 1. The graft copolymerization of styrene and MMA in DPNR latex was carried out based on the previous styrene-DPNR (recipe 1) and MMA-DPNR systems (recipe 2) [13, 14]. From table 1, it has been observed that polymerization of MMA monomer in styrene-DPNR system (recipe 3) is less stable and resulted in low monomer conversion of about 50 %. However, higher conversion (97.5 %) was achieved when polymerizing styrene in MMA-DPNR system (recipe 4). Thus, MMA-DPNR recipe was chosen for the polymerization of styrene and MMA in DPNR latex due to the high monomer conversion achieved for both styrene and MMA monomers. The more stable of styrene and MMA monomers in MMA system might due to the lower total solid content (TSC) employed in the system.

**Table 1. Recipe, reaction condition and the conversion for the polymerization**

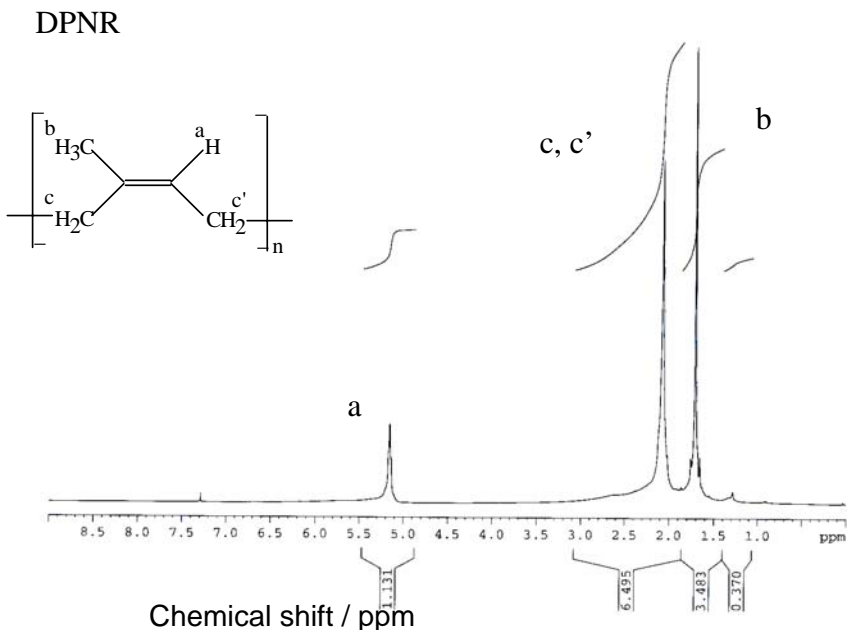
Recipes & reaction conditions	1*	2**	3	4	5	6	7
Styrene: MMA: Rubber ratio	25:0:75	0:20:80	0:25:75	20:0:80	10:10:80	10:10:80	10:10:80
Initiator concentration (per wt. of monomers, %)	2	5	2	5	5	5	5
TSC (%)	40	21	40	21	21	21	21
Reaction Temperature (°C)	60	65	60	65	65	65	65
Reaction Time (hours)	6	4	6	4	4	5	6
Conversion (%)	97.1	>99	50	97.5	91.3	96.5	>99

\* based on previous styrene-DPNR recipe

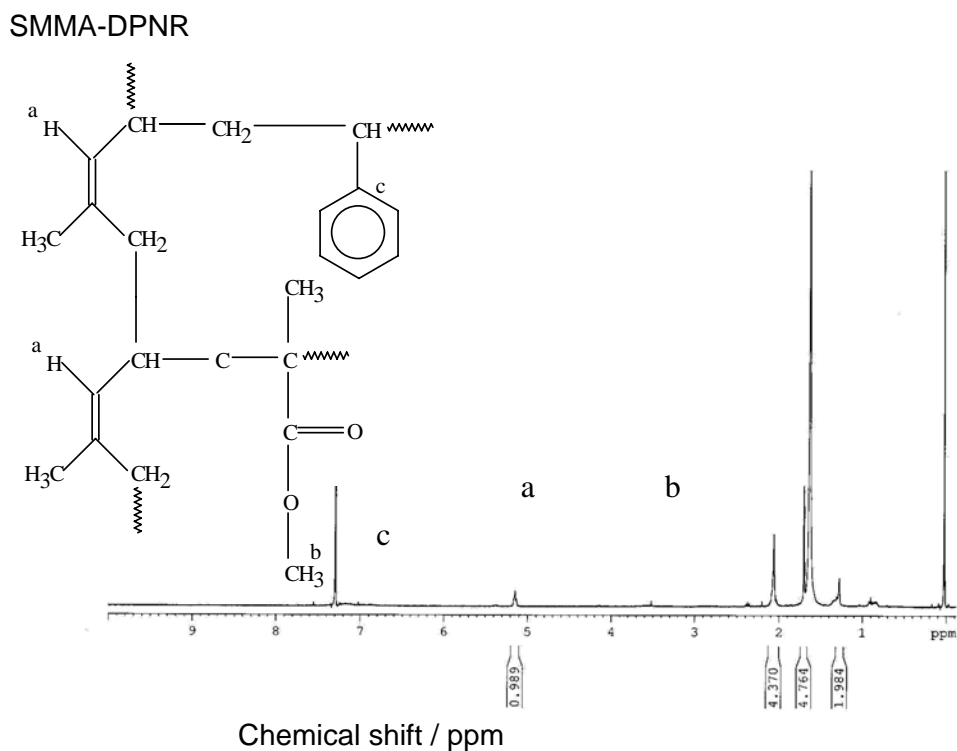
\*\* based on previous MMA-DPNR recipe

Polymerization of styrene-MMA in DPNR at 4 hours reaction time (recipe 5) yields a conversion of 91.3 % which is low and less efficient. Therefore the reaction time was prolonged to 5 and 6 hours (recipe 6 and 7) and managed to attain higher monomer conversion. This may be because increasing the reaction time; the radicals will have more time for participating in the reaction and as a result, increase the conversion to some extent. Further increase of reaction time to 6 hours (recipe 7) resulted in highest conversion i.e. >99 % and was later chosen to be used throughout the analysis

**<sup>1</sup>H NMR Spectra**



**Figure 1: <sup>1</sup>H NMR spectrum of no modified DPNR**



**Figure 2: <sup>1</sup>H NMR spectrum of DPNR grafted with Styrene and MMA**

The <sup>1</sup>H NMR spectra of DPNR and SMMA-DPNR are shown in Fig. 1 and Fig. 2, respectively. For DPNR, the unsaturated methyne proton show singlet resonance signal at 5.15 ppm (a). The peak at 2.10 may be attributed to the methylene protons (c, c') and the resonance signal of the methyl proton appears at 1.70 ppm (b).

The  $^1\text{H}$  NMR spectrum of SMMA-DPNR is shown in Figure 2. The unsaturated methyne proton (a) of the NR shows resonance at 5.15 ppm. The methoxy proton (b) of the acrylic group of the grafted MMA unit appears at 3.5 ppm and the peak of phenyl group (c) of PS observed at 7.1 ppm.

### **Copolymer Composition**

The  $^1\text{H}$  NMR technique is a well-established method for the determination of copolymer composition. The compositions of styrene and MMA units in the copolymer were determined from the integrated peak area of the corresponding protons in  $^1\text{H}$  NMR spectra. The molar composition for each copolymer of styrene and MMA were obtained and quoted as an average value [6,8]:

For styrene composition,

$$S_o = 1y, \text{ so } y = S_o$$

$$S_1 = 5x, \text{ so } x = \frac{S_1}{5}$$

$$C = \left[ \frac{\frac{S_1}{5}}{S_o + \frac{S_1}{5}} \right] \times 100 \quad (2)$$

Where

NR = y;

Styrene = x;

$S_o$  = integrated peak area value of the unsaturated methyne proton;

$S_1$  = integrated peak area value of the phenyl group of polystyrene unit;

C = % molar of monomer in the copolymer.

For MMA composition,

$$S_o = 1y, \text{ so } y = S_o$$

$$S_1 = 3x, \text{ so } x = \frac{S_1}{3}$$

$$C = \left[ \frac{\frac{S_1}{3}}{S_o + \frac{S_1}{3}} \right] \times 100 \quad (3)$$

Where

NR = y;

MMA = x;

$S_o$  = integrated peak area value of the unsaturated methyne proton;

$S_1$  = integrated peak area value of the

methoxy proton of MMA unit;  
 $C$  = % molar of monomer in the copolymer.

Then, the mass composition was calculated according to the following equation:

$$C' (\%) = \frac{(MM \times C)}{[(MM \times C + NR \times 100 - C)]} \quad (4)$$

Where

$MM$  = molecular mass of MMA  
 (100 g/mol) or styrene (96 g/mol);  
 $NR$  = molecular mass of  
 cis-1,4-polyisoprene (168 g/mol).

**Table 2: SMMA-DPNR copolymer composition**

copolymer	So	S1	C (%)	C' (%)
Styrene	0.54	0.28	9.40	12.78
MMA	0.54	0.14	7.96	11.28

Summary of the copolymer composition produced is given in Table 2. From Table 2, it can be seen that the amount of styrene ( $C'$ ) in the graft copolymers is slightly higher than that of MMA which were 12.78 and 11.28 g, respectively, although a similar amount of monomers (styrene / MMA) were initially used. The amount of styrene in the SMMA-DPNR copolymer is expected to be higher due to the higher reactivity of the styrene monomer compared to MMA. The reactivity of styrene ( $0.73 \pm 0.05$ ) is largely higher than MMA ( $0.19 \pm 0.05$ ) [8, 15-16], thus resulted in more active styrene monomers added to the NR backbone and formed a stable polymeric radical. The similar finding was also reported when polymerizing styrene and MMA onto NR latex [8].

## CONCLUSIONS

The conclusions that can be drawn from this research are:

1. Graft polymerization of styrene and MMA in DPNR latex using ammonium peroxy disulfate was successfully prepared with more than 99 % conversion at 6 hours reaction time.
2. The composition of styrene and MMA in the SMMA-DPNR copolymer was calculated and found to be 12.78 wt% and 11.28 wt%, respectively. The higher amount of styrene in the copolymer as compared to MMA was attributed to the higher reactivity ratio of styrene monomers.

## REFERENCES

1. Blackley, D. C. *Polymer Latices Science and Technology*, 2<sup>nd</sup> Edition, 1997. Chapman & Hall: London.
2. Ceresa, R. J. *Block and Graft Copolymerization*, vol. 1, 1973. Wiley, New York.
3. Hourston, D. J. & Romaine, J. 1989. Modification of natural rubber latex. I. Natural rubber-polystyrene composite latices synthesized using an amine-activated hydroperoxide. *Eur.Polym.J.* Vol 25, 695-700.

4. Hourston, D. J. & Romaine, J. 1990. Modification of natural rubber latex. II. Natural rubber poly(methyl methacrylate) composite latexes synthesized using an amine-activated hydroperoxide. *J.Appl.Polym.Sci.* 39, 1587-1594.
5. Hourston, D. J. & Romaine, J. 1991. Modification of natural rubber latex. III. Natural rubber-polyetyrene composite latexes synthesized using azobisisobutyronitrile as initiator. *J.Appl.Polym.Sci.* 43, 2207-2211.
6. Oliveira, P. C., Oliveira, A. M., Garcia, A., Barboza, J. C. S., Zavaglia, C. A. D. & Santos, A. M. 2005. Modification of natural rubber: A study by H NMR to asses the degree of graftization of polyDMAEMA or polyMMA onto rubber particles under latex form in the presence of a redox couple initiator. *Eur.Polym.J.* xx, xxxx
7. Arayaprane, W., Prasassrakich, P. & Rempel, G. L. 2002. Synthesis of graft copolymers from natural rubber using cumene hydroperoxide redox initiator. *J.Appl.Polym.Sci.* 83, 2993-3001.
8. Arayaprane, W., Prasassrakich, P. & Rempel, G. L. 2003. Process variables and their effects on grafting reactions of styrene and methyl methacrylate onto natural rubber. *J.Appl.Polym.Sci.* 89, 63-74.
9. Zhou, M. H., Hoang, T., Kim, I. G., Ha, C. S. & Cho, W, J, 2001. Synthesis and properties of natural rubber modified with stearyl methacrylate and divinylbenzene by graft polymerization. *J.Appl.Polym.Sci.* 79, 2464-2470.
10. Neoh, S. B. & Hashim, A. S. 2004. Highly grafted polystyrene-modified natural rubber as toughener for polystyrene. *J.Appl.Polym.Sci.* 93, 1660-1665.
11. Nakason, C., Kaesaman, A. & Yimwan, N. 2003. Preparation of graft copolymers from deproteinized and high ammonia concentrated natural rubber lattices with methyl methacrylate. *J.Appl.Polym.Sci.* 87, 68-75.
12. Nguyen, V. T., Abd. Kadir, M. O. & Hashim, A. S. 2002. A comparative study of styrene polymerization in deproteinized and undeproteinized natural rubber latex. *Rubber.Chem.Technol.* 75(1), 111-118.
13. Nguyen, V. T. 2000. Polystyrene-modified natural rubber from in situ polymerization of styrene in deproteinized natural rubber latex. Ph.D thesis, Universiti Sains Malaysia.
14. Ragvinger, S. J. 2000. Pempolimeran emulsi MMA; homopempolimeran dan pempolimeran in situ dalam lateks getah asli ternyahprotinkan. Master tesis. Universiti Sains Malaysia.
15. Huang, N. J., Sunberg, D. C. 1995. Fundamental studies of grafting reactions in free radical copolymerization. I. A detailed kinetic model for solution polymerization. *J Polym Sci Part A Polym Chem.* 33, 2533-2549.
16. Huang, N. J., Sunberg, D. C. 1995. Fundamental studies of grafting reactions in free radical copolymerization. II. Grafting of styrene, acrylate and methacrylate monomers onto cis-polybutadiene using AIBN initiator in solution polymerization. *J Polym Sci Part A Polym Chem.* 33 2551-2570.