

# Properties of Styrene-Methyl Methacrylate Grafted DPNR Latex at Different Monomer Concentrations

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**ABSTRACT:** The graft copolymerization of styrene and methyl methacrylate (MMA) on to deproteinized natural rubber (DPNR) latex was carried out. The effect of monomer concentrations on grafting efficiency, thermal and mechanical properties was studied. The synthesized graft copolymers were characterized by proton nuclear magnetic resonance (<sup>1</sup>H NMR) and the highest grafting efficiency was found at 20 wt % monomer concentration. At low monomer concentration (10 wt %) the grafting was not significant and at 30 wt %, the grafting efficiency was slightly decreased. The thermal properties of graft copolymers were analyzed using differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA). The degradation temperature ( $T_{deg}$ ) of the graft copolymer was

increased with the increase in monomer concentration which indicates the improvement in thermal stability. The DSC result showed improvement in miscibility between the components as the monomer concentration increased. The mechanical properties of gum and filled modified NR were also investigated in terms of tensile strength, tensile modulus and elongation at break. The tensile strength and elongation at break decreased with an increase in monomer concentration while tensile modulus increased as the monomer concentration increased. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 9–15, 2008

**Key words:** DPNR latex; styrene; methyl methacrylate; graft copolymerization; grafting efficiency

## INTRODUCTION

Natural rubber (NR) is an important material with unique characteristics used in a wide range of engineering applications, i.e. tire, rubber springs, vibration mounts etc.<sup>1,2</sup> Despite of the increase in research on synthetic rubbers, natural rubber remains a practically irreplaceable elastomer. The fact that it comes from a renewable source, coupled with the good properties, signifies that it is an important elastomeric material.<sup>3</sup>

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 have been developed to modify its properties through physical and chemical modifications. The inherent incompatibility at the molecular level poses by physical modification has been the main reason why chemical modifications of NR have gain interest among researchers. Among the famous types of modifications includes bond rearrangement, grafting and attachment of new chemical groups onto the

NR backbone.<sup>3,4</sup> Typical example of successful modified NR include Epoxidized Natural Rubber (ENR), which has currently been produced in pilot-plant quantities in Malaysia<sup>1</sup> and Polymethyl Methacrylate grafted natural rubber which was first introduced in mid 1950s under the trade name of Heveaplus.<sup>5</sup>

The grafting of NR with various monomers such as acrylonitrile, methyl methacrylate (MMA), stearyl methacrylate (SMA), divinylbenzene (DVB) and styrene using a range of initiator systems have been extensively studied.<sup>6–10</sup> It was found that MMA and styrene are the most suitable monomers for grafting to yields high level of grafting. Recently, grafting of binary mixtures of monomer has gained interest among researcher. In this regard, synergism during copolymerization reaction has been studied and investigated.<sup>11</sup> The graft copolymerization of styrene and MMA onto NR<sup>12</sup> and SBR latex<sup>13</sup> were also reported. Chemical reactions or grafting directly of monomers onto NR latex also can be influenced by the presence of the proteins. These proteins could act as free radical scavengers and terminate the free radicals species during the polymerization reaction and reduced the grafting efficiency. With respect to this low grafting efficiency and protein allergy issues,<sup>14</sup> therefore, DPNR is an obvious choice in graft copolymerization.<sup>11,15</sup>

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**TABLE I**  
**Recipe and Reaction Conditions for the Modified DPNR**

Recipe	10 wt %	20 wt %	30 wt %
DPNR latex (g)	228.8	203.4	203.4
Monomer (g)			
Styrene	7.5	15	22.5
Methyl methacrylate	7.5	15	22.5
Initiator (g)	0.75	1.5	2.25
Water (g)	471.7	485.6	499.6
<i>Parameter and reaction conditions</i>			
Styrene: MMA: Rubber ratio	5 : 5 : 90	10 : 10 : 80	15 : 15 : 70
Initiator concentration (per wt. of monomers, %)	5	5	5
TSC (%)	21	21	21
Reaction temperature (°C)	65	65	65
Reaction time (h)	6	6	6

The purpose of this work was to investigate the graft polymerization of styrene and MMA monomers onto DPNR latex particles using emulsion polymerization technique at different monomer concentrations, 10, 20, and 30 wt %. The reaction polymerization was carried out using ammonium peroxy disulfate ( $N_2H_8O_8S_2$ ) as the initiator. The initiator produces radicals that can be used to initiate polymerization, occurring either on the rubber backbone or on the monomer to be grafted. The radicals formation on the rubber backbone results in graft polymerization while radicals formation on the monomers results in homopolymerization. In this study, the low protein and non-rubbers content presence in DPNR latex used proved to provide higher radicals formation on the rubber backbone thus providing improved grafting efficiency. Consequently after the polymerization reaction, the grafting efficiency of the prepared graft copolymers was determined using  $^1H$  NMR. The effects of monomer concentrations on thermal and mechanical properties of the modified rubber were also investigated.

## EXPERIMENTAL

### Materials

The DPNR latex used was supplied by Sumirubber Industries (Malaysia) Sdn. Bhd. The dry rubber content (DRC) of DPNR latex was 59 wt % with nitrogen content of 0.047 wt %. The low amount of nitrogen indicates that the latex is highly deproteinized. The latex also contains 0.65 g/1  $H_2O$  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 due to its slightly water-soluble

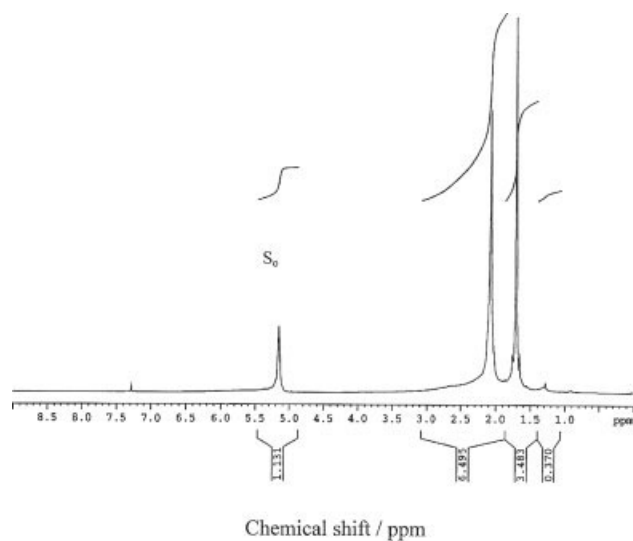
characteristic. Both the styrene and MMA monomers were kept in a refrigerator prior to use. The initiator, ammonium peroxy disulfate ( $N_2H_8O_8S_2$ ) was also purchased from Fluka Chemical Company. Deionised and distilled water were used throughout the work. The curatives used for rubber vulcanization were zinc oxide (activator), stearic acid (activator), *N*-isopropyl-*N*-phenyl-*p*-phenylendiamine (IPPD) (antioxidant), Dibenzothiazol disulfide (MBTS) (accelerator), sulfur (cross link agent) and carbon black type HAF N330 (filler).

### Preparation of grafted NR

The graft polymerization of styrene and MMA in DPNR latex was carried out in a 1 L reaction vessel according to the recipe and reaction conditions shown in Table I. 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 min. The mixture of styrene and MMA monomer were fed to the reactor drop-wise until the addition's completed. 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. 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 such as leaching process for 24 h with three times of water changing and drying to the constant weight under vacuum at 50°C was carried out to remove any water soluble impurities.<sup>16</sup>

### Solvent extractions

Several components or substances are expected to exist in this gross polymer sample. Ungrafted poly (methyl methacrylate) (PMMA), polystyrene (PS)



**Figure 1**  $^1\text{H}$  NMR spectrum of unmodified DPNR.

and poly(styrene-*co*-methyl methacrylate) (PS/PMMA) are referred to as free copolymers. The possible graft copolymers produced are DPNR grafted MMA (DPNR-*g*-PMMA), DPNR grafted styrene (DPNR-*g*-PS) and DPNR grafted styrene-MMA (DPNR-*g*-PS/PMMA). The grafting efficiency was calculated using the following equation:

$$\text{Grafting efficiency (\%)} = \frac{\text{Total weight of monomers grafted (g)}}{\text{Total weight of monomers polymerized (g)}} \times 100 \quad (1)$$

The free or ungrafted copolymers St and MMA were washed out in the following Soxhlet extractor using mixture solvents of acetone and methyl ethyl ketone (MEK) (1 : 1 by volume) for 24 h. Weights of the initial samples and the extracted samples were measured for the determination of graft copolymer and free copolymer content. The extracted samples were then used for the  $^1\text{H}$  NMR analysis.

### $^1\text{H}$ NMR analysis

The grafting efficiency has been evaluated by  $^1\text{H}$  NMR. The samples of unmodified DPNR and modified DPNR at 10, 20, and 30 wt % monomer concentrations were swollen for 12 h in deuterated chloroform and analyzed by  $^1\text{H}$  NMR in a 400 MHz spectrometer (Bruker) at 20°C.

### Differential scanning calorimeter analysis

Glass transition temperature ( $T_g$ ) of the modified DPNR at 10, 20, and 30 wt % monomer concentration was determined by DSC analysis. DSC used for this test was Perkin Elmer model DSC7. The heating rate and temperature range for the analysis were

10.0°C/min and room temperature to 150°C, respectively.

### Thermal gravimetry analysis

The thermal behaviour of DPNR and modified DPNR at 10, 20, and 30 wt % monomer concentration was determined by TGA analysis. The experiments were carried out in a TGA7 Perkin Elmer. The heating rate and temperature range for the analysis were 20.0°C/min and from room temperature to 600°C, respectively.

### Tensile tests

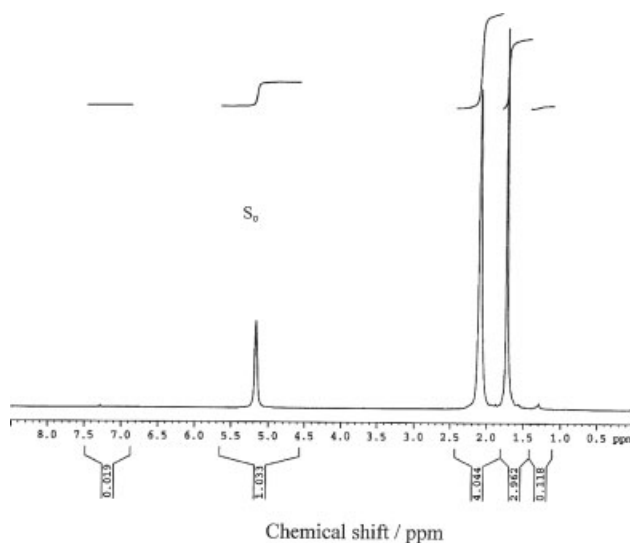
The modified DPNR prepared was compounded on a two-roll mill using a typical semi-efficient sulphur formulation. The tensile properties of the rubber vulcanizates were measured using Testometric Instron M5000-25 KN. Tensile testing of the samples was performed at  $25 \pm 2^\circ\text{C}$  at a crosshead speed of 500 mm min<sup>-1</sup> according to ASTM D 412.

## RESULT AND DISCUSSIONS

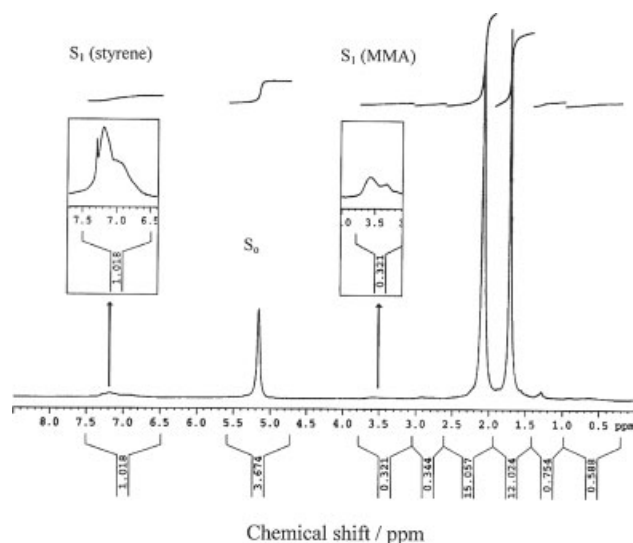
### $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR spectra of DPNR and modified DPNR at 10, 20, and 30 wt % monomer concentrations are shown in Figures 1–4, respectively. For DPNR, the unsaturated methyne proton shows singlet resonance signal at 5.15 ppm. The peak at 2.10 ppm may be attributed to the methylene protons and the resonance signal of the methyl proton appears at 1.70 ppm. The peak for solvent (deuterated chloroform) was observed at 7.3 ppm.

The  $^1\text{H}$  NMR spectra of modified DPNR at different monomer concentrations are shown in Figures 2–4. For



**Figure 2**  $^1\text{H}$  NMR spectrum of modified DPNR at 10 wt % monomer concentration.



**Figure 3**  $^1\text{H}$  NMR spectrum of modified DPNR at 20 wt % monomer concentration.

10, 20, and 30 wt % monomer concentrations, the unsaturated methyne proton of the DPNR shows resonance at 5.15 ppm. For 10 wt % monomer concentration, no peak was observed for phenyl group of PS and methoxy proton of the acrylic group of the grafted MMA. At 20 and 30 wt %, the peaks for phenyl group of PS unit appear at 7.1–7.3 ppm and a not so pronounce peak of methoxy proton of the acrylic group of the grafted MMA appears at 3.6 ppm. The signals obtained were in good agreement with the previous studies which reported that the signal of phenyl group of PS and the methoxy proton of the acrylic group of PMMA appears at 6.5–7.5 ppm and 3.5–3.7 ppm, respectively.<sup>12,17,18</sup> Hence, these  $^1\text{H}$  NMR analysis have confirmed the presence of grafted styrene and MMA in the in the modified DPNR prepared.

### Degree of grafting

The graft copolymer of styrene and MMA units in the modified DPNR was determined from the integrated peak area of the corresponding protons in  $^1\text{H}$  NMR spectra and automatically calculated by the instrument software. The molar and mass composition for graft copolymer of styrene and MMA onto DPNR in Table II were obtained according to the following equations<sup>12,17</sup>:

For styrene composition,  $S_0 = 1y$ , so  $y = S_0$ ,  $S_1 = 5x$ , so  $x = \frac{S_1}{5}$

$$C = \left[ \frac{\frac{S_1}{5}}{S_0 + \frac{S_1}{5}} \right] \times 100 \quad (2)$$

where  $\text{NR} = y$ ; Styrene =  $x$ ;  $S_0$  = integrated peak area value of the unsaturated methyne proton;  $S_1$  = integrated peak area value of the phenyl group of styrene unit;  $C$  = % molar of monomer in the copolymer.

For MMA composition,  $S_0(a) = 1y$ , so  $y = S_0$ ,  $S_1(e) = 3x$ , so  $x = \frac{S_1}{3}$

$$C = \left[ \frac{\frac{S_1}{3}}{S_0 + \frac{S_1}{3}} \right] \times 100 \quad (3)$$

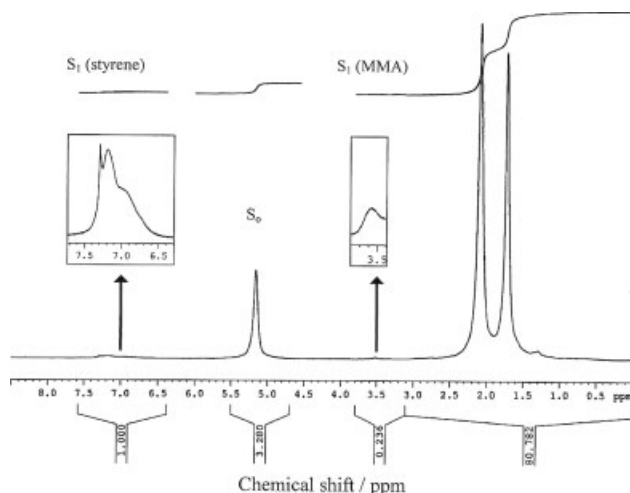
where  $\text{NR} = y$ ; MMA =  $x$ ;  $S_0$  = integrated peak area value of the unsaturated methyne proton;  $S_1$  = integrated peak area value of the methoxy proton of MMA unit;  $C$  = % molar of monomer in the copolymer.

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

$$C'(\%) = \frac{(\text{MM} \times C)}{[(\text{MM} \times C + \text{NR} \times 10 - C)]} \quad (4)$$

where  $\text{MM}$  = molecular mass of MMA (100 g/mol) or styrene (96 g/mol);  $\text{NR}$  = molecular mass of cis-1,4-polyisoprene (68 g/mol).

Grafting efficiency was evaluated based on mass composition obtained in Table II. Figure 5 shows the effect of monomer concentration on grafting efficiency. At 10 wt % monomer concentration, the grafting between St-MMA and DPNR was not significant and not detectable. The grafting efficiency increases as the monomer content increased, up to 20 wt % and decreases with further addition of monomer (30 wt %). At higher monomer concentrations, there were many reactions that probably competed with the graft copolymerization. Therefore, homopolymerization was more pronounced than graft copolymerization at higher monomer concentrations. Moreover, there were no new active sites on the rubber molecules for the newly arriving active monomers. This was because of the limitation of the cis-1,4-configuration and the grafting sites on the cis



**Figure 4**  $^1\text{H}$  NMR spectrum of modified DPNR at 30 wt % monomer concentration.

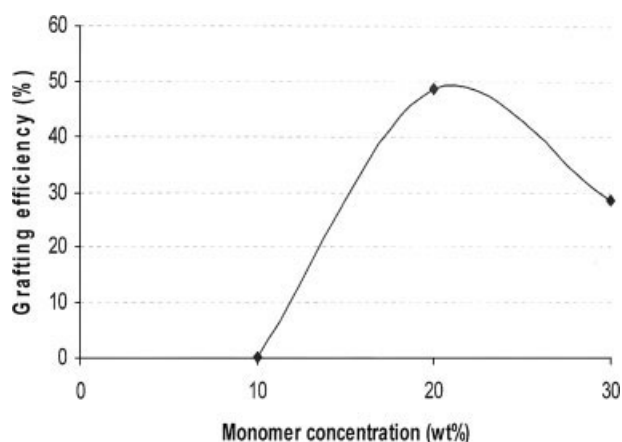
**TABLE II**  
Copolymer Composition of Modified DPNR

Copolymer	$S_0$	$S_1$ (styrene)	$S_1$ (MMA)	C% (St and MMA)	C' % (St and MMA)
10 wt%	1.033	–	–	0	0
20 wt%	3.674	1.018	0.321	7.760	10.810
30 wt%	3.280	1.000	0.236	7.832	10.910

positions might not be available after a certain percentage of grafting took place.<sup>15</sup> Also, as grafting proceeds and a certain shell thickness of the polymer is reached, the contact area between monomer and rubber decrease. Therefore, it is more difficult for graft copolymerization to occur through diffusion of the monomer to the rubber chain, compared to the homopolymerization or copolymerization of monomers. As a result, the degree of grafting decreases with increasing monomer to rubber ratio.<sup>12</sup>

#### Differential scanning calorimeter analysis

Differential scanning calorimetry (DSC) can be used for the evaluation of the miscibility between components of copolymers. In the absence of miscibility, a composite of two polymers exhibits two distinct glass transitions of the pure components. Figure 6 shows the DSC curves of modified DPNR at 10, 20, and 30 wt % monomer concentrations. At 10 wt % monomer concentration, two peaks were clearly observed at 124 and 130°C which might due to the presence of copolymer of PS and PMMA respectively. No pronounced peak was observed at 20 and 30 wt % monomer loading and this indicate the low amount of un-grafted copolymer of PMMA and PS presence in the modified rubber. The differences also might attributed to the higher amount of PMMA and PS grafted to the rubber backbones in 20 and 30

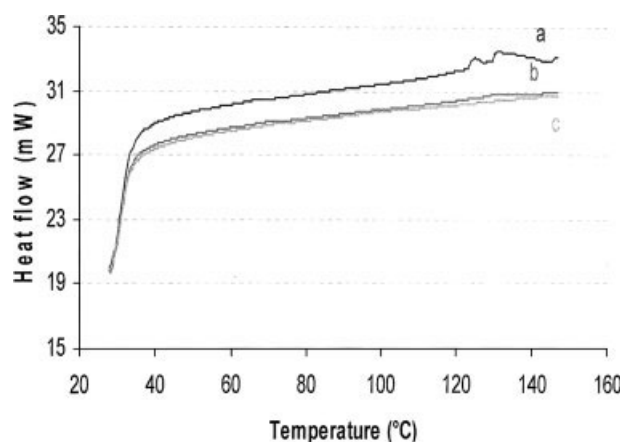


**Figure 5** Effect of monomer concentration on grafting efficiency of modified DPNR.

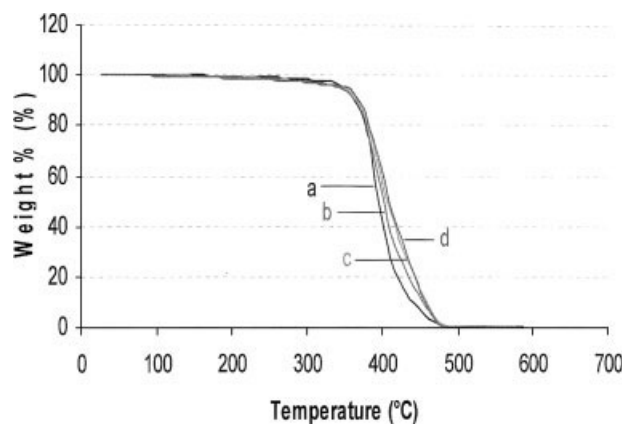
wt % compared to 10 wt % monomer loading. However the expected glass transition temperature ( $T_g$ ) (around 60°C) of grafted rubber is not pronounced due to the dominant of NR molecules. Arayapraneet al.<sup>17</sup> reported that the  $T_g$  of secondary transition peak which belong to copolymers phase decreased in intensity and area with an increasing grafting efficiency.

#### Thermal gravimetry analysis

The thermogravimetric analysis (TGA) curves of DPNR (a) and modified DPNR at 10 (b), 20 (c), and 30 (d) wt% monomer concentrations are shown in Figure 7. The figure shows that there is a considerable change in the thermal behaviour of the rubber upon monomer concentration. The degradation temperatures of grafted NR were considerably higher than unmodified NR and are shown in Table III. The increases in degradation temperature of the modified DPNR were expected due to the presence of PS and PMMA as well as grafted structure in the modified DPNR which generally resulted in an increase in the chain stiffness of the modified rubber and contribute to improved thermal properties. As the monomer contents increases, the degradation temperature of the rubbers were also increase accordingly.



**Figure 6** DSC curve of (a) 10, (b) 20 and (c) 30 wt % monomer concentrations of modified DPNR.



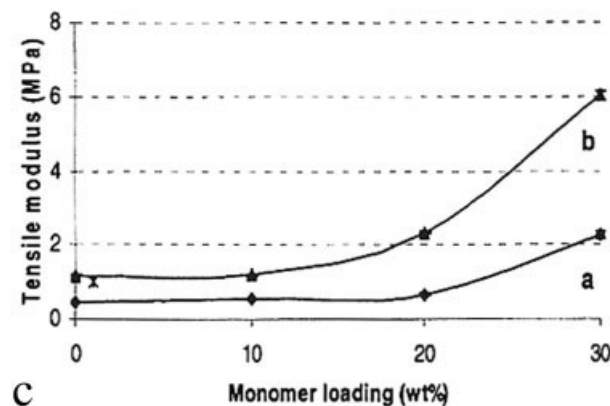
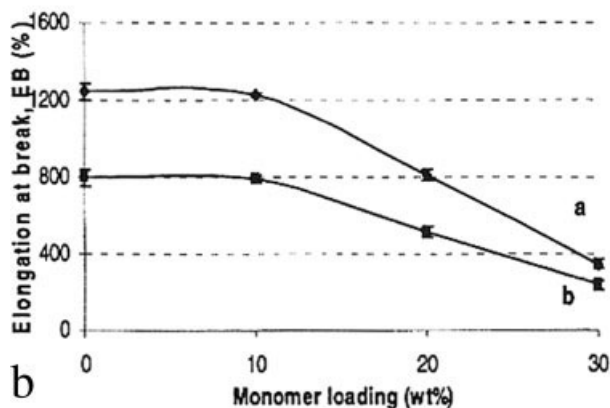
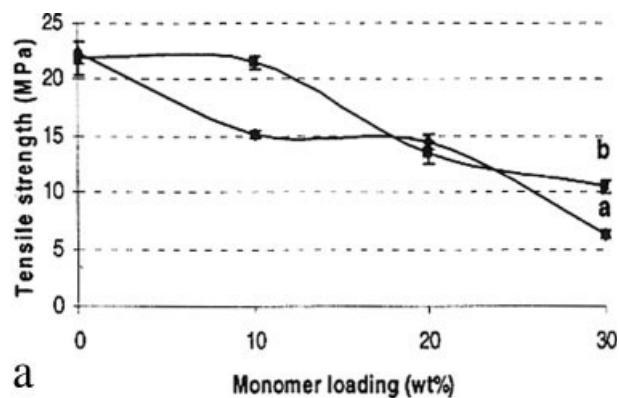
**Figure 7** Temperature versus weight curve for (a) DPNR, and modified DPNR at (b) 10 wt %, (c) 20 wt %, and (d) 30 wt % monomer percentages.

### Tensile properties

Figure 8 shows the effect of monomer concentrations on tensile strength (8a), elongation at break (8b) and tensile modulus (8c) of gum (a) and filled (b) DPNR and modified DPNR. The incorporation of the PS and PMMA has raised the modulus and reduced the elongation at break. The tensile strength of the modified rubber also reduced. The similar trends were observed for both gum and filled vulcanizates. The reduction in tensile strength and elongation at break is probably due to the less effective fusion of hard rubber particles of high modulus and due to reduced tendency for strain crystallization on stretching as the close packing of molecular segments is restricted by the grafted chain. The presence of the hard PS and PMMA has reduced the elasticity of rubber chains which resulting in more rigid and stiffer vulcanizates. Polar attraction between grafted molecules is another factor contributes to the increased in modulus. The addition of carbon black into the rubber also resulted in higher modulus and tensile strength and reduces the elongation at break as compared with gum vulcanizate due to the reinforcement effect of the filler.

**TABLE III**  
Degradation Temperature for DPNR and Modified DPNR

Sample	Degradation temperature (°C)
DPNR	395.55
10 wt%	395.59
20 wt%	397.39
30 wt%	398.07



**Figure 8** Effects of monomer concentrations on tensile strength (8a), elongation at break (8b) and tensile modulus (8c) of gum and filled DPNR and modified DPNR.

### CONCLUSION

The graft copolymerizations of styrene and MMA onto DPNR latex at different monomer concentrations were successfully prepared. It has been observed that the grafting efficiency has increased with the increase in monomer concentration and slightly decreased with further addition of monomer. The highest grafting efficiency was found at 20 wt % monomer concentration. Thermal stability of the graft copolymer prepared was improved and degradation temperature increased with the increase in

monomer loading. The DSC results shows improvement in miscibility between the components as the monomer concentration increased. The incorporation of the PS and PMMA has raised the modulus and reduced the elongation at break as well as tensile strength of the modified rubber. The similar trends were observed for both gum and filled vulcanizates.

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