MECHANICAL PROPERTIES AND THERMAL STABILITY OF METHYL METHACRYLATE GRAFTED LATEX AND NATURAL RUBBER LATEX FOAM BLENDS

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Abstract

Graft copolymerization has been and is still globally used as one of the main methods of modifying natural rubber in both latex form and solution. Plenty of researches can be found on the application of graft copolymerization to reinforce natural rubber latex, but research on incorporating grafted rubber into natural rubber latex foam (NRLF) is yet to be done. The purpose of this study was to investigate the effect of methyl methacrylate grafted rubber latex (MGL) loading on the mechanical properties of the compounded NRLF. The blended latex was prepared by mixing high ammonia natural rubber latex and the industry-standard polymethyl methacrylate (PMMA)-grafted natural rubber latex, referred to as MG49. Then, the blended latex was compounded and processed into NRLF at a laboratory scale via the Dunlop process. A comparative study between the NRLF produced with varying MGL percentage, i.e., 0% (control), 10%, 20%, 30%, 40% and 50% was done. The hardness, compression set and stiffness of the NRLF increased as the percentage of MGL content in the NRLF increased. The addition of MGL in the NRLF showed a decrease in the thermal stability of the NRLF for temperatures below 400 °C, but no significant trend for higher temperatures. NRLF samples with higher MGL content also showed a tendency to swell more when soaked in toluene.

Keywords: Grafted rubber latex, Natural rubber latex foam, Methyl methacrylate.
1. Introduction

Natural rubber latex foams (NRLF) are cellular rubbers produced by the in-situ generation of gas in the polymer. The production of moulded latex foam started with the discovery of combined whipping and controlled gelling process by the Dunlop Rubber Company [1]. The process involves the whipping of a latex compound, which has been de-ammoniated and matured, followed by the addition of a gelling agent. The delayed action gelling agent, sodium silicofluoride, can set the foam in a few minutes at room temperature [2]. The foamed latex is then transferred to the mould and vulcanised in an oven. The major applications of NRLF are as cushioning material in furniture, bedding and automotive industries. The number of air cells present in the foam, their average size and how they intercommunicate determines the properties of the latex foam such as density, compressive behaviour and water absorption.

The additions of a controlled amount of mineral fillers, biocomposites and synthetic polymers on NRLF have shown to improve its hardness and other important physical properties. Despite lowering the cost and improving some properties, high loading of fillers affects the bodyweight of foamed products, i.e., they are too dense to handle in selected applications, such as in mattresses. Rubber latex foam prepared from modified natural rubber may provide a certain degree of reinforcement to important physical properties. The grafting of an olefinic monomer like acrylonitrile, methyl methacrylate, and styrene onto natural rubber is carried out to enhance the polarity of the new chemical groups on the NR backbone and to improve the filler-rubber interaction [3]. The weights of these foams are, therefore, lower and less dense compared to NRLF produced using conventional filler loading methods. The latex foam product would also provide a lower risk of allergic reactions caused by proteinaceous matter present in the natural rubber latex [4].

Latex blending is a technique commonly employed to obtain a combination of desirable characteristics inherent in the individual polymer and to enhance the properties of the final product [5]. Natural rubber latex is favoured for its high strength, flexibility and elasticity. However, it is also known to have inferior properties such as low heat, oxygen and ozone resistance, poor wet grip properties and poor oil resistance [6]. Grafted natural rubber latex compensates for these weaknesses by reinforcing the unsaturated natural rubber latex structure, but it has poor film-forming and is harder to process [7].

Methyl methacrylate-grafted natural rubber latex, more commonly referred to as methyl methacrylate rubber latex (MGL), is a speciality latex formed through graft copolymerization of methyl methacrylate monomer with NRL. The industry standard graft copolymer of MG rubber contains 49% polymethyl methacrylate, more commonly labelled as MG49. Through grafting, the rigid chains of polymethyl methacrylate are embedded onto the flexible chains of natural rubber, giving MG rubber self-reinforcing properties. However, MG rubber has poor film-forming properties and processing options. Lu et al. [8] and Su’ait et al. [9] indicated that by mixing natural rubber latex and grafted natural rubber latex to form NRLF may give rise to materials with new properties and applications.

This study was done to test the feasibility of using MGL as a reinforcing agent in NRLF to replace conventional industry-standard fillers. The aim was to find out if a quality NRLF can be produced by preparing blends of natural rubber latex and
methyl methacrylate-grafted natural rubber latex via Dunlop process. MGL was added to natural rubber latex in varying ratios to produce compounded NRLFs, and the mechanical properties were tested.

2. Materials and Methods

The Dunlop process was used to produce latex foam rubber with a different blend of NRL and MGL following the formulation shown in Table 1 based on the dry rubber weight. The high ammonia NRL and the PMMA-grafted natural rubber latex (MG49) was provided by Getahindus (M) Sdn. Bhd., and used as received. The other chemicals such as Zinc Diethyldithiocarbamate (ZDEC), 2-Mercaptobenzothiazole (MBT), Sulphur, Potassium oleate soap, 1,3-Diphenylguanidine (DPG), Zinc Oxide (ZnO) and Sodium Silicofluoride (SSF) were obtained from LGC Scientific Sdn. Bhd. Details of the compound formulation used to produce the NRLFs were shown in Table 2.

Table 1. NRL and GRL content in NRLF samples prepared (%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Control</th>
<th>10%</th>
<th>20%</th>
<th>30%</th>
<th>40%</th>
<th>50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%) NRL</td>
<td>100</td>
<td>90</td>
<td>80</td>
<td>70</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td>(%) MGL</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 2. Formulation for preparation of natural rubber latex foam.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Total solid content (%)</th>
<th>Formulation* (p.h.r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRL/NRL-GRL blends</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Zinc Diethyldithiocarbamate (ZDEC)</td>
<td>67</td>
<td>1</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole (MBT)</td>
<td>67</td>
<td>1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>Potassium Oleate soap</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>1,3-Diphenylguanidine (DPG)</td>
<td>40</td>
<td>0.3</td>
</tr>
<tr>
<td>Zinc Oxide (ZnO)</td>
<td>50</td>
<td>1.5</td>
</tr>
<tr>
<td>Sodium Hexafluorosilicate (SSF)</td>
<td>20</td>
<td>1</td>
</tr>
</tbody>
</table>

First, the latex blend was stirred for 5 minutes using the Elba ESMB-D5515(GR) stand mixer. Then, vulcanizing agent (Sulphur) and foaming agent (potassium oleate soap) were added to the mixture while stirring at low speed. MBT and ZDEC accelerators were added to the mixture after 2 hours of stirring. Consequently, the latex compound was left to mature at room temperature for 15 hours with continuous low-speed stirring. After 15 hours of maturation, latex compound was thoroughly beaten and foamed until the volume increased up to three to four times of the initial volume. The foaming speed was subsequently decreased to obtain a fine and even foam with evenly sized air bubbles.

Gelling agents such as DPG and ZnO were added into the foamed compound while vigorous beating was continued for another 90 seconds. Secondary gelling agent SSF was added and the mixing continued for a further 90 seconds. Finally, the un-gelled foam was immediately transferred into a mould and left at ambient temperature. When the gelling set, the foam was cured in a hot air oven at 100 °C for 2 hours. The foam was removed from the mould after curing and rinsed thoroughly with deionized water to remove potassium oleate soap, non-reacted
elements and other residues. The rinsed latex foam was then dried in a hot air oven at 80 °C for 8 hours.

3. Characteristics of Samples

Given that the main application of rubber foam is as cushioning material, various mechanical characteristics under compression such as stress-strain behaviour, recovery, hardness, thermal stability, swelling behaviour and microscopic study of the samples were conducted. Six samples were prepared for each of the testings.

3.1. Measurement of compressive stress-strain behaviour

The Lloyd universal testing machine was used to perform the compression test. The ASTM D3574 standard procedure was used to study the compression behaviour of the NRLF samples. As per the requirement, the samples were prepared in a cubic form with a dimension of 50×50×25 mm. The specimen was compressed up to 50% of the original thickness at a compression speed of 0.83 ± 0.08 mm/s. The initial and final thickness after the compression was recorded and the stress-strain curves were obtained.

3.2. Measurement of compression set and recovery

Samples were prepared and the experiment was carried out according to the ASTM D3574 standard. The samples were compressed to about 75% of its initial thickness with a clamp. The compressed NRLFs were then transferred to an oven with a temperature of 70 °C for 24 hours. 24 hours later, the samples were removed from the oven, allowed to cool, unclamped and measured for its compression properties, i.e., constant deflection compression set and recovery percentage.

3.3. Measurement of hardness

The hardness of the samples was determined using the Shore Hardness Durometer A test 59-500-111. The indentation foot was brought into contact with the surface of the NRLF. A constant force was applied on the surface of the NRLF. The samples prepared were tested 3 times each and the average results were calculated.

3.4. Measurement of thermal stability

PerkinElmer STA6000 Thermogravimetry TGA-DSC Instrument was used to conduct thermogravimetric analyses on the samples. Testing of the samples was conducted under nitrogen gas with a heating rate of 20 °C /min from 30 °C to 600 °C. Weight loss of the samples as a function of temperature was obtained.

3.5. Measurement of swelling

The swelling test was carried out to determine the susceptibility of the samples to moisture. The compounded NRLF samples were cut into 45 mm diameter circles, weighed and immersed in toluene. The samples were immersed in a closed bottle for 72 hours at room temperature. Then the samples were removed, cleaned with a dry cloth and weighed. The samples were weighed again after drying in an oven at 70 °C for 15 min. Equation 1 was used to obtain the amount of Toluene uptake per gram rubber hydrocarbon, Q.
\[ Q = \frac{M_3 - M_2}{M_1 \times \frac{M_4}{100}} \]  

where \( M_1 \) = original mass, \( M_2 \) = swollen mass, \( M_3 \) = dried mass and \( M_4 \) = formula mass.

### 3.6. Scanning electron microscopy

The morphologies study of the samples were investigated by scanning electron microscopy (SEM) using FEI QUANTA 400F scanning electron microscope. Small cubic shaped samples with the size of 20 mm were cut from the latex foams and the morphological properties of the rubber compounds were studied. Magnifications of 80 times were obtained for each sample. The surfaces of the samples were covered with thin layers of palladium, Pd, to prevent electron charging of the samples when the scanning was in progress.

### 4. Results and Discussion

Figure 1(a) shows the control NRLF prepared from 100% natural rubber latex without the addition of MGL. The NRLF prepared with lower percentages of MGL showed relatively better surface appearance compared to NRLF prepared with a higher percentage of MGL. This is because the surfaces of the NRLF with higher MGL percentage appear to have the formation of cracks. This is particularly obvious on the NRLF with 50% MGL content where there was significant crack formation as shown in Fig. 1(b). A similar study done by Nakason et al. [4] reported appearances of cracked surfaces for compounds prepared from deproteinized natural rubber and PMMA grafted latex especially copolymers with high PMMA content. 

The SEM micrographs obtained are shown in Fig. 2. All the NRLF samples can be seen to exhibit an open cell structure. The variation in pore size of the open cell structure decreases as the percentage of MGL content in the NRLF increases as seen from Figs. 2(b) to (d). This finding coincides with the increment in compression strength and hardness of the NRLF as MGL content in the NRLF is increased. With the addition of MGL, the density of the foam increases. A similar trend was reported by Sanhawong et al. [10] that incorporated concentrated natural rubber latex (CNRL) into biofoam products. In addition, Bashir et al. [11] observed a similar trend with NRLF incorporated with eggshell powder, where a decrease in pore size variation was observed with increasing eggshell powder content.

(a) Control.  
(b) 50%.

Fig. 1. NRLF samples.
Fig. 2. SEM for NRLF samples.

The results for the hardness test conducted are shown in Fig. 3. From Fig. 3, the shore A hardness of the NRLF increased with increments in the percentage of MGL in the NRLF. According to Bashir et al. [11], this observation could be caused by the nature of the PMMA grafted latex and the demobilizing effect of PMMA on the polymer chain. The PMMA grafted latex, in film form, is harder than the polymer matrix. Thus, the hardness increases with the MGL content. A similar trend was reported by Arayapranee and Rempel [12] who incorporated styrene-GNR into NR.

Figure 4 depicted the compressive stress-strain curves for the NRLF compounds. The stress-strain curves show that compressive stress increases as the amount of MGL increases. This can be attributed to a formation of good interfacial interaction between the polymethyl methacrylate (PMMA) molecules in the grafted rubber latex and the high ammonia natural rubber latex used to make the latex blend. This interaction inhibits the movement of the polymeric chain, thus, making the compounded NRLF samples stiffer and less elastic. By increasing the amount of MGL used in the compounded latex to form the NRLF, more PMMA molecules are present in the latex blend. This increased presence of PMMA molecules causes
the increase in stiffness of the NRLF as the percentage of MGL is increased. To further support the findings from the compression test, a study done by Ramasamy et al. [13] attributed the increase in stiffness of their rice husk powder filled NRLF to an enhancement in the interaction of the filler matrix, further supported by the morphological studies done in the report.

![Fig. 3. Hardness of NRLF samples.](image3)

![Fig. 4. Compressive stress-strain relationship of NRLF samples.](image4)
The compression set tests were done to measure the elastic behaviour of the samples. From a study conducted on the compression set of TDI polyurethane foams, Sonnenshein et al. [14] stated that the compression set of natural rubber latex foams depend on the molecular structure. These molecular structures are the open cell structures of the NRLF. Open-cell structures are the polymer structures that were formed during polymerization in the foaming process. Van der Schuur et al. [15] determined that significant differences in compression set values could arise from modifications in the formulation of the material. From Fig. 5, the lowest compression set value was shown by the control sample with no MGL content. The low compression set values translate to the high elasticity of the NRLF. The compression set values increased as NRLFs with higher MGL content were tested. From Fig. 6, the control sample displayed the most recovery percentage in the shortest amount of time. Increasing MGL content in the NRLF samples showed a subsequent decrease in recovery percentage. Van der Schuur et al. [15] also credited the deformation of the hard phase as the main factor for non-elastic deformation. The increased presence of PMMA in the polymer chains caused an increase in hardness of the NRLF, hence, the decrease in recovery percentage.

![Fig. 5. Constant deflection compression set of NRLF samples.](image1)

![Fig. 6. Recovery percentage (%) of NRLF samples.](image2)
Thermal stability is a very important trait in NRLFs. Strength, toughness and elasticity of the NRLF may change according to the temperature it is subjected to. Specific applications require specific understanding of how the NRLFs react in different temperatures [16]. Figure 7 shows the results obtained from the thermogravimetric analysis done on the NRLF samples and Table 3 summarizes the TGA results. From the graph, weight change in percentage of the NRLF samples with increasing temperature under nitrogen gas can be obtained. From Table 3, at 5% weight loss, the thermal stability of the samples decreased as the MGL content in the NRLF increased. The control NRLF experienced 5% weight loss at a temperature of 298.11 °C, whereas the 50% MGL NRLF showed 5% weight loss at 258.61 °C, with the samples in between showing a similar trend. This trend continued at 30% weight loss, with the control NRLF again showing the highest temperature and the 50% MGL NRLF showing the lowest temperature, with the other samples experiencing a steady decrease in thermal stability as MGL percentage increased. However, for higher temperatures, a significant trend could not be identified based on the results obtained from the TGA tests. This implies that the addition of MGL in the NRLFs lowers the thermal stability for temperatures below 400 °C, but does not affect the thermal stability for higher temperatures. Notably from the results, the NRLF samples are suitable for applications at a temperature lower than 350 °C without thermal degradation.

![Fig. 7. Effect of temperature on weight of NRLF samples.](image)

<table>
<thead>
<tr>
<th>NRLF sample</th>
<th>Temperature at 5% weight loss</th>
<th>Temperature at 30% weight loss</th>
<th>Maximum weight loss</th>
<th>Temperature at maximum</th>
<th>Weight of char</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>298.11</td>
<td>378.09</td>
<td>92.27</td>
<td>588.93</td>
<td>7.73</td>
</tr>
<tr>
<td>10%</td>
<td>285.83</td>
<td>374.49</td>
<td>90.65</td>
<td>589.29</td>
<td>9.35</td>
</tr>
<tr>
<td>20%</td>
<td>279.23</td>
<td>374.14</td>
<td>91.52</td>
<td>588.74</td>
<td>8.48</td>
</tr>
<tr>
<td>30%</td>
<td>263.31</td>
<td>372.37</td>
<td>91.32</td>
<td>588.94</td>
<td>8.68</td>
</tr>
<tr>
<td>40%</td>
<td>266.39</td>
<td>374.08</td>
<td>92.27</td>
<td>589.96</td>
<td>7.73</td>
</tr>
<tr>
<td>50%</td>
<td>258.61</td>
<td>369.14</td>
<td>91.17</td>
<td>589.53</td>
<td>8.82</td>
</tr>
</tbody>
</table>
From Fig. 8, it can be observed that the swelling increased with increasing MGL content. The control NRLF showed the least swelling while the highest percentage of swelling was shown by the 50% MGL content NRLF sample. The expansion level of the NRLF contributed to an increase in the swelling. The increase in the swelling percentage can be attributed to an increase in molecular compactions at the interface between the mould and NRLF samples. This would cause the layer in contact to have a higher density at the grain boundary. This is further explained in a study by Lee et al. [17], which stated that the swelling of natural rubber sponge is influenced by the cell structure and the density.

In summary, it can be seen that the incorporation of MGL into the NRLF samples affected the mechanical properties in a different manner. While the stiffness, hardness, compression set and susceptibility to swelling increases, the recovery and thermal stability below 400 °C decrease with the amount of MGL content. Depending on the applications, the properties of NRLF products can be tuned by varying the amount of MGL in the blend.

![Swelling of NRLF samples](image)

**Fig. 8. Swelling of NRLF samples.**

5. Conclusion

The NRLF was determined to have an open cell structure from the micrographs obtained from the scanning electron microscope. The stress-strain curve from the compression test showed that Young’s modulus of the NRLF increased as the MGL content in the foam increased. As expected, the control NRLF had the lowest stiffness. The general trend was an increase in the stress value of the NRLF as percentage of MGL in the foam increased, implying that an increase in MGL increases hardness but makes the NRLF less elastic. This was further supported by the compression set and recovery percentage tests that were carried out. The addition of MGL in the NRLF showed a decrease in the thermal stability of the NRLF for temperatures below 400 °C. However, the addition of MGL in the NRLF did not yield an improvement in the thermal stability of the NRLF for temperatures higher than 400 °C. Increasing the percentage of MGL did not affect the thermal stability of the samples significantly for temperatures above 400 °C. NRLF samples with higher MGL content also showed a tendency to swell more when soaked in toluene. Overall, the use of MGL as a reinforcing agent to replace natural fillers is a viable option depending on the application of the NRLF.
Acknowledgement

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<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>CNRL</td>
<td>Concentrated natural rubber latex</td>
</tr>
<tr>
<td>DPG</td>
<td>1,3-Diphenylguanidine</td>
</tr>
<tr>
<td>MBT</td>
<td>Mercaptobenzothiazole</td>
</tr>
<tr>
<td>NRLF</td>
<td>Natural Rubber Latex Foam</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl Methacrylate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SSF</td>
<td>Sodium Silicofluoride</td>
</tr>
<tr>
<td>ZDEC</td>
<td>Zinc Diethyldithiocarbamate</td>
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</table>

References

2. Murphy, E.A.; and Owen, E.W.B. (1929). Improvements in or relating to the manufacture of goods of rubber or similar material. GB332526A, Dunlop Rubber Co. Ltd, United Kingdom.


