Correlation of Open Cell Structure with Properties of Green Rubber Foam from Epoxidised Natural Rubber/Reclaimed Rubber Glove

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ABSTRACT

A promising impact absorber foam material was produced from epoxidised natural rubber (ENR) and reclaimed rubber (RR) with the addition of sodium bicarbonate (SBC) as a blowing agent. This study is part of our effort to develop green rubber foam from reclaimed rubber from glove. It focuses on the effect of different ENR/RR ratio of 100/0, 90/10, 70/30, 50/50, 30/70 and 0/100. The samples were prepared by melt compounding using a Haake internal mixer and expanded via two step heat transfer foaming process. The physical characteristics (expansion ratio, density and water absorption) and impact absorption by drop ball testing of ENR/RR foams were studied. The results showed significant correlation between the rubber blend ratios with generated pore structures towards the properties of the foams. From the experimental values, ENR/RR with the ratio of 90/10 yielded the rubber foam with the highest relative density of 0.85 as well as the lowest water absorption rate of 0.1 g/hrs. This foam cell characteristics resulted in
improved energy absorption behaviour. Sample with optimum pore size of ~0.36 mm shows the highest energy absorption of up to 0.65 joules compared to others.

**Keywords:** ENR/RR blends, foams, physical properties, energy absorption.

**Introduction**

There is growing interest for rubber materials in industrial and commercial applications. One of the major demands is rubber foam which is also known as cellular, sponge or expanded rubber [1, 2]. Rubber foam is widely applied for footwear, stereo earphones, speaker surrounds, goggles, orthopaedic soft goods, carpet anti-skid cushioning, cycle seats, etc. which are commonly require good cushioning, excellence shock absorption, elasticity and resistance to fatigue properties. All these properties are attainable from rubber materials due to their high tear and tensile strength, high abrasion resistance and durability [2]. Reclaimed rubber (RR) is one initiative for reducing the environmental problem and at the same time to produce products with significant properties at lower cost. Nowadays, there are increasing awareness among researchers to reduce environmental and health issues to overcome the consumption of mineral based materials in their studies [3].

A substance that produces a cellular structure in a polymer mass is defined as a blowing agent [4]. Chemical blowing agents for polymer are available in a wide range of formulations depending on the polymer processing temperature and the decomposition temperature of the blowing agent. Referring to Yamsaengsung et al. [5] and Karak [6], the gas release temperature of blowing agent should match the processing temperature of the polymers for optimum foaming. Several findings suggested N,N’-dinitiosopentam (H) [7], sodium bicarbonate (SBC), 4,4’oxybis (benzenesulfonylhydrazide) (OBSH) [5], azodicarbonamide (AZD) [5], zinc carbonate (ZnCO3), etc. as a foaming agent.

In this present work, the effect of ENR: RR blend ratio towards the pore structure and physical properties of rubber foam was studied. It includes the evaluation on energy absorption efficiencies of the rubber foam via a drop ball impact test methodology with respect to the pores’ morphology. The findings were further supported by the optical microscopy (OM) observation.
Methodology

Materials and sample preparation
For the preparation of ENR/RR foam, epoxidised natural rubber (ENR) and reclaimed rubber (RR) were blended along with sodium bicarbonate (SBC) as a gas-producing agent. A semi-EV system consisted of 100 phr (part per hundred rubber) ENR/RR, 4 phr zinc oxide, 2 phr stearic acid, 2.5 phr tetramethyl thiuram disulfide (TMTD), 1 phr benzothiazyl-2-cyclohexyl-sulfenamide (CBS) and 1.0 phr sulfur was utilised. All the materials were used as received except for pre-preparation stage by drying and crushing using an agate mortar. Compound (Figure 1) was prepared using a Haake internal mixer working at 60°C and a rotor speed of 60 rpm in accordance to ASTM D-3182. A heat transfer foaming technique was used for the vulcanization and foaming process. The two-stages involved are, 1 minute of compression molding at the temperature of 100°C for pre-vulcanization and was followed by simultaneous curing and foaming in an air-circulating oven for 30 minutes at 150°C. Various ratio of ENR/RR were used for the preparation of ENR/RR compounds; 100/0, 90/10, 70/30, 50/50, 30/70, 0/100.

Figure 1: (a) ENR/RR blend after compounding, (b) Molded rubber and (c) Rubber foam

Sample characterisation
Expansion ratio: It was measured in accordance with ASTM D3575-93. Initially, rubber compound for different formulation was hot pressed at 100°C to a sheet of 20x20x10mm. Initial height, $H_o$ and height after foaming at 150°C, $H_f$ was determined. The foam expansion ratio was calculated based on the following Eq. (1):

$$\text{Expansion ratio} = \frac{H_f - H_o}{H_o}$$

(1)
Relative density: The relative density of the foam was measured in accordance to ASTM D-1056 by using Eq. (2) as given:

\[
\text{Relative density} = \frac{\text{Foam density (g/cm}^3\text{)}}{\text{Solid density (g/cm}^3\text{)}}
\]  

(2)

Water absorption, \(W_{abs}\): Water absorption test was conducted in accordance to ASTM C-1083 to determine the amount of water absorbed under specified conditions. The 20x20x10 mm samples were dried in an oven for a period of 3 hrs at temperature of 60°C and then placed in a desiccator to cool down to room temperature. Immediately upon cooling the specimens were weighed. The material is then immersed in 450 ml water at 25°C ± 3°C for 24 hours. After that, specimens were removed, blotted dry with a lint free cloth, and then weighed. Water absorption rate was calculated based on following Eq. 3:

\[
W_{abs} = \text{Final weight} - \text{Initial weight}
\]  

(3)

Impact by drop test: The impact test by falling weight was performed by a 0.14 kg mass sphere ball impactor. The ball was dropped from a height, \(H_1\) of 540 mm onto a 30x30 mm sample. The height of the first rebound, \(H_2\) was measured and the energy absorption (in unit of joule, J) was calculated as Eq. 4:

\[
\text{Potential energy, } E = \text{Mass} \times \text{Gravity acceleration} \times (H_2 - H_2)
\]  

(4)

Foam pore morphology: The optical microscopy (OM) was used to investigate the pore structure of ENR/RR foam. The average cell size and number of pores were determined and the shapes were analysed qualitatively.

**Result and Discussion**

Table 1 shows the expansion ratio of rubber foam at different ENR/RR ratio. It is clearly observed that expansion ratio increases with the increasing RR content in the blend. This is highly contributed by the generated morphology of the foam structures which affected by the ratio of ENR to RR blend. The expansion ratio showed good agreement with the relative density of the foams (Figure 2a). According to Ariff et al. [8] increasing cell size and thinning effect of the cell wall will directly alter the foam density as well as foam expansion ratio. Relatively, the foam density is reduced and the ratio of foam expansion will also increase.
Table 1: Expansion ratio of ENR/RR foams at different ratio

<table>
<thead>
<tr>
<th>Sample ENR:RR (phr)</th>
<th>Height before foaming (mm)</th>
<th>Height after foaming (mm)</th>
<th>Expansion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>14.48</td>
<td>15.04</td>
<td>0.039</td>
</tr>
<tr>
<td>90/10</td>
<td>14.48</td>
<td>16.17</td>
<td>0.117</td>
</tr>
<tr>
<td>70/30</td>
<td>14.48</td>
<td>23.43</td>
<td>0.618</td>
</tr>
<tr>
<td>50/50</td>
<td>14.48</td>
<td>25.71</td>
<td>0.776</td>
</tr>
<tr>
<td>30/70</td>
<td>14.48</td>
<td>32.98</td>
<td>1.278</td>
</tr>
<tr>
<td>0/100</td>
<td>14.48</td>
<td>36.53</td>
<td>1.523</td>
</tr>
</tbody>
</table>

Figure 2(a) shows the decrease of relative density of rubber foam with the increase of RR content. This is due to the lower ability of the RR to be re-vulcanised. In a rubber foam, crosslinking will form a network consisting of higher packing polymer chain and results in increasing foam relative density [8]. However in this case, higher RR content with lower tendency for new crosslinking provides loose sites for the carbon dioxide (CO\textsubscript{2}) gases to stretch the pore wall created by sodium bicarbonate in the ENR/RR mixture. The expansion of the pore walls resulted in a relatively larger pores’ sizes with irregular shapes and thus produces foam with lower relative density. Furthermore, the amount of virgin rubber per unit volume is reduced, and thus less crosslinking is presence.

Figure 2(b) depicts the increase of water absorption rate of foam with the increase of RR content. Higher content of RR allowing the foam to expand and consequently producing a foam with large unfilled space. Moreover, opened cell structures of ENR/RR foam increased the affinity of the foams towards water. Thus, more water is absorbed into the unsaturated part of the foam.

The efficiency of impact absorption of the rubber foam is a compromise between the ENR/RR ratio and the foam structure. The resultant value of impact absorption is inversely proportional to the pore size. From Figure 3, sample with 90/10 ENR/RR ratio contributes to the highest impact absorption value with the smallest pores dimension compared to other samples (not considering the reference sample of ENR/RR 100/0 and 0/100). An optimum pore size capable of absorbing the highest energy whereas larger pore structure in a sample is believed to exhibit higher plasticity. There are various factors that influence the foam morphology such as temperature, pressure, polymeric materials and the formulations used [8]. In this study, the pore distribution and size varies with the percentage of RR in the foam (Figure 4).
Figure 2: (a) Relative density and (b) Water absorption for different ENR/RR ratio

Figure 3: Impact energy absorption for various ENR/RR ratio

The correlation between energy absorption and pore characteristics (sizes and number of pores/volume) are summarised in Figure 5. The energy absorption is observed to decrease exponentially with the increase of pore diameter. The sample 90/10 manifested the highest energy absorption with the smallest pore diameter as well as the highest pore density if compared to the other foams. The lowest energy absorption was shown by 0/100. In
contrast, this 0/100 sample exhibited the lowest pore density with the largest pore diameter. This scenario reflected the importance of pore characteristics as well as morphology towards the energy absorption of the foam. The presence of ENR phase in the foam produced pores with spherical-like shapes with increasing irregularity with the increased of RR component. The presence of RR was found to weaken the damping properties of epoxidised natural rubber foam when subjected energy was converted to mechanical energy rather than been absorbed by the materials. The energy absorption pattern of these foams are in close relation with the morphological characteristics of the foams (Figure 4).

Figure 4: Optical micrograph of (a) 100/0, (b) 90/10, (c) 70/30, (d) 50/50, (e) 30/70, and (f) 0/100 samples. The scale is 0.5mm
The optimum pore size absorbs higher impact energy. A foam with higher pore density capable to dissipate impact energy whereas, spherical shape pores could contribute to the recovery properties related with the elasticity of the foam materials. Throughout this study, it is observed that incorporation of RR in a foam decreases the energy absorption capability due to the lower pore density as well as irregular pore shapes. Furthermore, the combination of large pore size and irregular shape pores could contribute to the plasticity of the foam which limits the recovery of the foam under load. However, it is interesting to note that incorporation of RR at 10 to 50 wt% had negligible effect to the decrement in energy absorption. This finding is significant for the development of green rubber foams for energy absorption application, cushion performance, buoyancy and others [9].

![Figure 5: Correlation between pore characteristics with energy absorption](image)

**Conclusions**

The experimental result indicates the effective ratio of ENR/RR affects the physical and energy absorption properties of the rubber foam. As the RR content increases, there are more sites for pore enlargements. This resulted in a foam with relatively lower density and higher water absorption rate due to
the enlargement of pores and decrease of crosslink density. In a drop ball testing, samples which absorbed more energy after impact caused the ball to bounce at a lower height after impact. The test revealed that samples with optimum pore size is applicable for an efficient energy absorption. This is in a good agreement with morphological characteristics of the foam structure. Sample with higher pore unit/volume and at an optimum diameter are essential for energy absorption. As a conclusion, it is revealed that higher fresh rubber content (ENR) has better tendency to produce a foam with higher pore density, lower pore size and consequently exhibit higher energy absorption than a mixture with higher reclaimed rubber (RR) content.

Acknowledgment

The authors acknowledge the Universiti Teknikal Malaysia Melaka for funding this research through the Short Term Research Grant Scheme with the project number of PJP/2013/FKP (8A) S01189.

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