

Effect of blowing agent type and blowing agent loading levels on mechanical and cell morphological properties of dry natural rubber cellular compounds

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Abstract

Cellular rubber is important in various industrial applications, due to its unique structural properties, such as its low density, cushioning performance, thermal and acoustic insulator properties and moderate energy absorption. In this study, the influence of blowing agent type and blowing agent loading levels on mechanical and morphological properties of cellular natural rubber were investigated. Three types of blowing agents namely NaHCO₃, DNPT and isopropanol were used. The cellular rubber compounds were prepared using a conventional compression molding technique via a heat transfer foaming process. The mechanical properties were evaluated according to ASTM standards and the results yielded were observed to systematically correlate with the morphology of cellular compounds. Uneven morphology was observed in the compounds with 10 phr for all three blowing agents owing to high gas content in the rubber matrix. Overall, most of the properties of the cellular rubber compounds gradually decreased upon increasing the blowing agent loading levels in terms of mechanical properties, relative density, water absorption and crosslink density. In addition, isopropanol incorporated compound had the lowest compression set properties.

Key words: blowing agent, cellular rubber, mechanical properties, morphology

Introduction

Cellular materials are currently used extensively in a wide variety of applications such as packaging and comfort materials like bedding or seating and as well as in energy absorption and heat transfer applications (Gibson *et al.*, 2010). Properties of cellular structures are dependent on various factors such as cell morphology,

cell density, geometric parameters, cell size, material characteristics and manufacturing processes as well as structural boundary and loading conditions for lower weight applications (Mazur *et al.*, 2016). Depending on their cellular structure, cellular materials can be classified in to two groups as closed and open cell structures (Kabir *et al.*, 2006) and they could be selectively

prepared by the proper selection of blowing agents (BAs), their loading and curatives to achieve the correct balance between the volume of gas generated and the degree of curing (Zakaria *et al.*, 2017). BA is the most important ingredient to make the cellular compound due to its gas generating ability within the polymeric materials as they are thermally decomposed into gases causing the cellular structure formation as temperature increases. However, the correct BA is selected for a polymer based on decomposition temperature, decomposition rate, particle size (surface area) and the gas generation capacity of the BA (Wagner, *et al.*, 2014). Typical gases released from blowing process are nitrogen, carbon monoxide and carbon dioxide (Sombatsompop *et al.*, 2000). In this study, three BAs namely sodium bicarbonate (NaHCO_3), Dinitrosopentamethylene tetramine (DNPT) and isopropanol were used. DNPT which is an organic BA with decomposition temperature of 190 °C was used as it is a BA widely used in the world for most of the commercial applications (Choi, *et al.*, 2006). Isopropanol is also an organic BA with the lower decomposition temperature (83 °C). Sodium bicarbonate is an inorganic BA which decomposes at 50°C producing CO_2 and H_2O and sodium carbonate (Tangboriboon *et al.*, 2015 and Kmetty *et al.*, 2018). Natural rubber (NR) was selected as the polymeric material in this study due its natural availability and

its renewable properties, in order to promote its usage replacing synthetic polymers, such as polyurethane.

It is evident from literature that a majority of studies focuses on rubber foam derived from latex and synthetic polymers lattices (Sombatsompop *et al.*, 2000). However, studies concerning dry rubber foams with the comparison of organic and inorganic BAs have not received much attention and dry rubber based cellular materials are considered to have rigid cellular structures compared to latex-based foams which can be used for wide variety of applications such as compressive bushes, automotive items, *etc.* Therefore, in this study, natural dry rubber based cellular material was prepared by varying the loadings of the above mentioned three types of BAs and their properties were investigated.

Experimental

Materials and Methods

The natural rubber used in this study was crepe rubber (1X), obtained from Rubber Research Institute of Sri Lanka. NaHCO_3 (w/w 99.9%), DNPT (w/w 99%) and isopropanol (w/w 99.9%) were purchased from Organic Trade (Pvt.) Ltd, Sri Lanka. All other rubber ingredients, such as sulphur (w/w 99.5%), zinc oxide (w/w 98%), stearic acid, tetramethyl thiuram disulphide (TMTD), white oil and diphenyl guanidine (DPG), were purchased from Glorchem Enterprise, Sri Lanka.

Preparation of dry rubber based cellular compounds

Three series of dry rubber based cellular compounds were prepared with three different types of BAs and by varying the BA loading from 2 to 10 phr at 2 phr intervals. The compound prepared with 6 phr loading of DNPT was considered as the Control. The formulations of the

compounds are given in Table 1. Compounding was carried out using a laboratory two-roll mill (6" x 13") (David Bridge & Co. Ltd. Castleton Rochdale, England). Total mixing time of the two roll mill was kept constant at 10 minutes. The mixing cycle used in the preparation of the dry rubber based cellular compounds is given in Table 2.

Table 1. Formulations of cellular compounds

Ingredient	Function	Part per hundred of rubber (phr)
Crepe rubber	Polymer	100
ZnO	Inorganic activator	5
Stearic acid	Organic activator	2
TMTD	Primary accelerator	1
DPG	Secondary accelerator	0.5
White oil	Paraffinic Processing oil	15
WSP	Antioxidant	1
Sulphur	Vulcanizing agent	1.5
Sodium bicarbonate	Inorganic BA	2/4/6/8/10
DNPT	Organic BA	2/4/6/8/10
Isopropanol	Organic BA	2/4/6/8/10

Table 2. Mixing cycle used in preparation of cellular compounds

Added ingredients/chemicals	Time (minutes)
Crepe rubber (NR)	0
ZnO + Stearic Acid + WSP	2
½ Blowing Agent + ½ White Oil	3
½ Blowing Agent + ½ White Oil	5
DPG	6
TMTD	7
Sulphur	8
Dump	10

Vulcanization and foaming process

The compounds were moulded with a hydraulic press (KAO-Tech compression moulding machine) for 20 min at a temperature of 150°C.

Characterization of cellular compounds

Mechanical properties

Tensile test

Tensile properties of cellular compounds were determined using the Instron tensile testing machine according to ASTM D3574. Dumbbell shaped tensile test specimens were used. Crosshead speed was maintained at 50 mm/min.

Compression set

The compression set of cellular compounds was evaluated according to ASTM D395, using following Equation 1.

$$\text{compression set\%} = \left(\frac{h_0 - h_1}{h_0 - h_n} \right) \times 100\% \dots\dots\dots 1.$$

Where, h_0 and h_1 are initial thickness and thickness after test of cellular compound respectively and h_n is the spacer thickness.

Relative foam density

The relative density of cellular compounds was measured according to ASTM D3575, using Equation 2 as given below:

$$\text{Relative density} = \frac{\text{Foam Density}}{\text{Solid Density}} \dots 2.$$

Crosslink density

The crosslink density was determined as per ASTM D471 standards. Three test specimens having dimensions of 30 mm × 1 mm × 2 mm were immersed in p-xylene for 24 hours in closed-lid bottles. The samples were then removed from the solvent, wiped thoroughly to remove excess solvent and weighed again; this value was taken as the swollen weight. The crosslink density of the sample was calculated using the Flory-Rehner equation given in Equation 3.

$$-\{\ln(1 - \mathcal{V}_r) + \mathcal{V}_r + \mathcal{X}\mathcal{V}_r^2\} = \rho\mathcal{V}_0 \mathcal{M}_c^{-1} \mathcal{V}_r^{1/3} \dots\dots\dots 3.$$

Where,

- \mathcal{X} = Interaction constant characteristic between rubber and xylene, 0.34
- ρ = Rubber density
- \mathcal{V}_0 = Molar volume of xylene
- \mathcal{V}_r = Volume fraction of rubber in swollen sample
- \mathcal{M}_c = Average molecular weight between crosslinks

The volume fraction of rubber in the swollen sample, \mathcal{V}_r is given by Equation 4.

$$\mathcal{V}_r = \frac{(x_r/\rho_r)}{(x_r/\rho_r) + (x_s/\rho_s)} \dots\dots\dots 4.$$

Where,

- ρ_s = Density of xylene
- ρ_r = Density of the raw rubber

X_s = Mass fraction of xylene,
which can be obtain
from Equation 5
 X_r = weight of the rubber,
given by equation 6

$$X_s = \frac{(\text{weight of swollen sample} - \text{original weight})}{\text{weight of swollen sample}} \dots 5.$$

$$X_r = 1 - X_s \dots \dots \dots 6.$$

Therefore, the value of M_c can be used to calculate the physical crosslink density, using Equation 7.

$$[X]_{phys} = \frac{1}{2M_c} \dots \dots \dots 7.$$

Cell morphology

Surface morphology of cellular compounds was examined by scanning electron microscopy (SEM) using a ZEISS EVO LS 15 microscope. The specimens were cut and mounted on aluminum stubs. The specimens were then sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

Water absorption

The water absorption was evaluated according to ASTM D570, using Equation 8 where initially the weight of the test specimens was measured and recorded (Dry weight). Then the specimens were emerged in distilled water for three days and the weight was measured (Wet weight). The test specimens were patted dry with a tissue paper before measuring the final weight.

$$\text{Water Absorption \%} = \frac{(\text{Wet Weight} - \text{Dry Weight})}{(\text{Dry Weight})} \times 100\% \dots \dots 8.$$

Data analysis

All three series of cellular compounds were subjected to the above physio – mechanical tests and obtained data were analyzed by using the Minitab 17 statistical software with the use of General Liner Model (GLM) with Dunnett comparison tests at 95% confidence interval. All the tests were replicated for three times at least and error bars have been calculated for the replicated results.

Results and Discussion

Mechanical properties

Figure 1 shows a decreasing trend in tensile strength with the increase BA loading for all three blowing agents investigated. This could be attributed to the increase in the free volume or air space generated at high BA loading resulting the cells to collapse in the final morphological structure (Fig. 7). Decrease in crosslink density as evident from the results presented in Figure 7 may have also contributed to this trend. The compounds prepared with 2 phr loading of BA showed a significantly high tensile strength when compared to that of other loadings. Further, compound prepared with 2 phr loading of isopropanol shows remarkable tensile strength compared to other cellular rubber types. In addition, as the BA loadings increased the gas phase of the compound increases resulting the cells to collapse in the final morphological structure (Fig. 7).

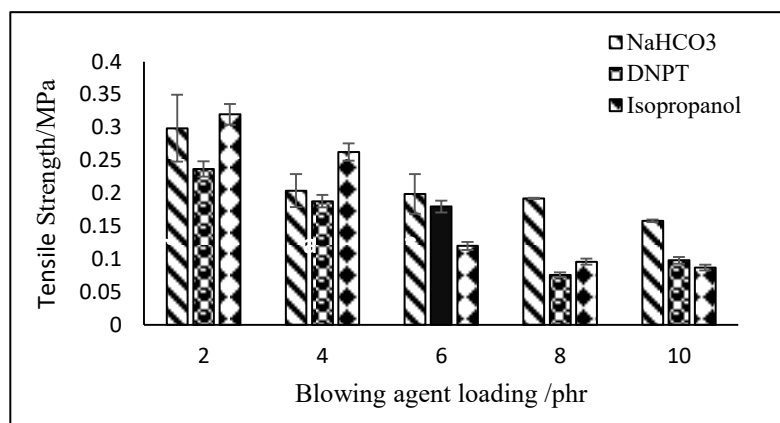


Fig. 1. Tensile strength of cellular rubber compounds

Figure 2 shows variation of elongation at break with different types of BAs and loadings. Elongation at break is an important physical parameter to explain the elastic behavior of the amorphous material. There is a decrease in trend on elongation at the break of NaHCO₃ and DNPT with the increase of BA loadings. In contrast, the results of the isopropanol incorporated compound indicate a fluctuating nature. The compound prepared with 2 phr loadings of NaHCO₃ shows better results compared to other BA loadings. This could be due to the better adhesion among the NR molecules. Figure 2

shows the surface morphology of 2 phr loading of the former three types of Bas and it shows that NaHCO₃ has large cells compared to isopropanol and DNPT. Similar morphological observation can be seen in the studies conducted by Najib *et al.*, (2009). It could be a possible reason for having high elasticity for the compound with NaHCO₃ BA. In contrast, the surface morphology of DNPT incorporated compound has high cell density at 2 phr loading. As a result, the elasticity of this compound is lower than NaHCO₃ and isopropanol.

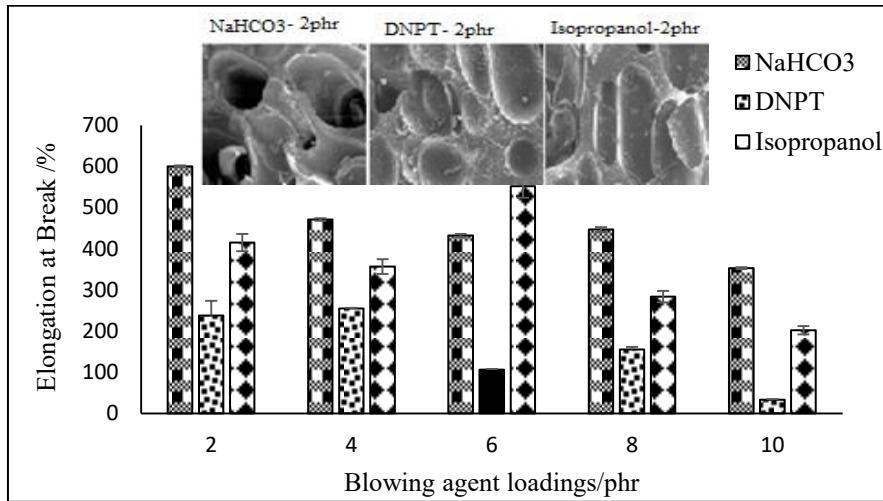


Fig. 2. Elongation at break of cellular rubber compounds

Modulus at 100% elongation is an important parameter to explain the hardness of a polymeric material (Gauthier, 1995). The compounds prepared with 4 phr loadings indicate the highest results for modulus at 100% elongation. Therefore, it might be the optimum loading to enhance the proper adhesion between NR and compounding ingredients. When the overall trend of modulus at 100% elongation is considered, an increment up to 4 phr loadings of BAs followed by a decline from 4 phr to 10 phr loadings were observed. At higher loadings of BAs, compounds indicate lower results of modulus at 100% elongation. There are number of possible reasons for this observation. The increase in the gas phase within the compound reduces the rubber phase by creating micro voids

which then reduces the strength of the compound compared to a compound without BAs. Additionally, with the increase in BA loading some of the cell walls can be fragmented leading to low strength structures within the compound. Another reason might be the possible agglomerates of the BAs at higher loadings which lowers the interfacial interactions between NR and BA. This is evident from the morphological studies carried out at 6 phr and 10 phr loading of the NaHCO_3 BA (Fig. 7). This observation enables ease of fractions to occur leading to a reduction in hardness. Further, similar results have been obtained in the study of property evaluation of cassava starch incorporated sponge based on NR (Temna *et al.*, 2014).

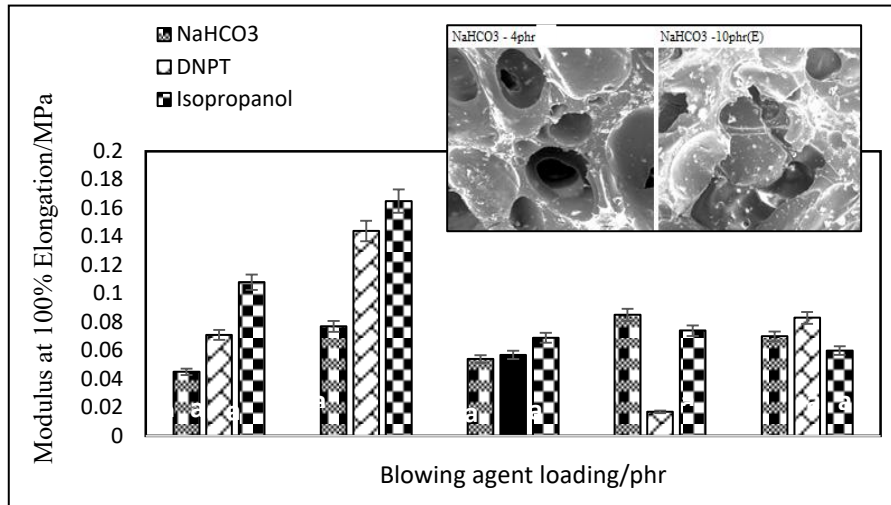


Fig. 3. Modulus at 100% elongation of cellular rubber compounds

According to Figure 4, a decreasing trend is observed in the compression set with increasing BA loading. This can be attributed to the number of cells generated when increasing the BA (Najib *et al.*, 2009). When the BA loading increases the number of cells within the structure is increased (Fig. 7). Therefore, a high amount of micro voids enables the compound to store more gas within the structure and release it when it is compressed. This helps to retain the elastic properties resulting in a decreasing trend in the compression set values for each BA. When comparing the results of different BAs NaHCO₃ has the highest compression

set values followed by DNPT and isopropanol compounds. The main reason for this observation can be the open/closed cell structures present in the compound. The air trapped within the closed cell structures helps it to bear the force to retain until it is released. However there is no such support in the case of open cell structure which then leads to possible breaking of the cell walls providing higher compression values when compared to closed cell structures. The study conducted by Tangboriboon, *et al.*, (2015) also reveals this trend with NaHCO₃ and DNPTBA.

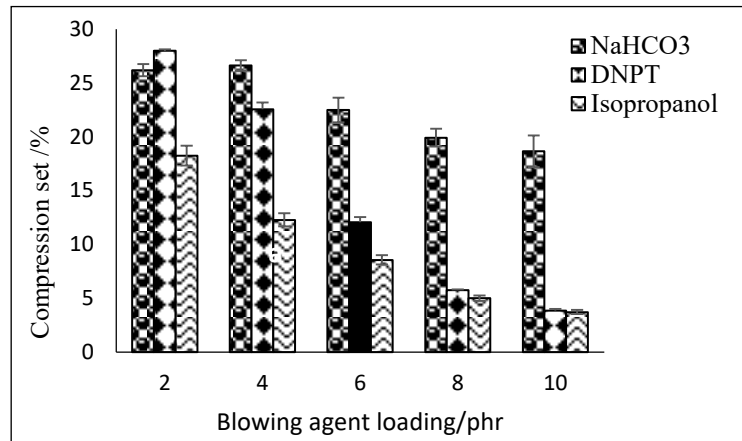


Fig. 4. Compression set of cellular rubber compounds

Relative density

Figure 5 illustrates the effect of the BA and BA loading on the relative density of the cellular rubber compound. It shows the relative density value decreased with increase in BA loading. As greater loadings of BAs were used, more gas was subsequently generated, reducing the relative density. Zakaria, (2007) reported that higher BA loadings shorten the growth time of the foam, thus restricting the gas from escaping through the foam surface, allowing the foam to expand more, and consequently, producing foam with a lower relative density. Further, NaHCO₃ has low relative density when compared to DNPT and isopropanol. In closed-cell structure, the gases are trapped in the

cells and the weight of the compound can be higher than the open cell structure. Additionally, the free volume in the compound with the NaHCO₃ BA is higher compared to the other two BAs due to its open cellular structure. When considering the types of gases evolved throughout the decomposition process the CO₂ gas evolved by NaHCO₃ and isopropanol is considered to be more soluble in the polymer material when compared to N₂ gas generated from DNPT, and as a result the DNPT containing compound can generate higher number of closed cells (Di Maio *et al.*, 2005). This leads to having lower densities with the cellular structures which are having CO₂ as the decomposition gas than N₂.

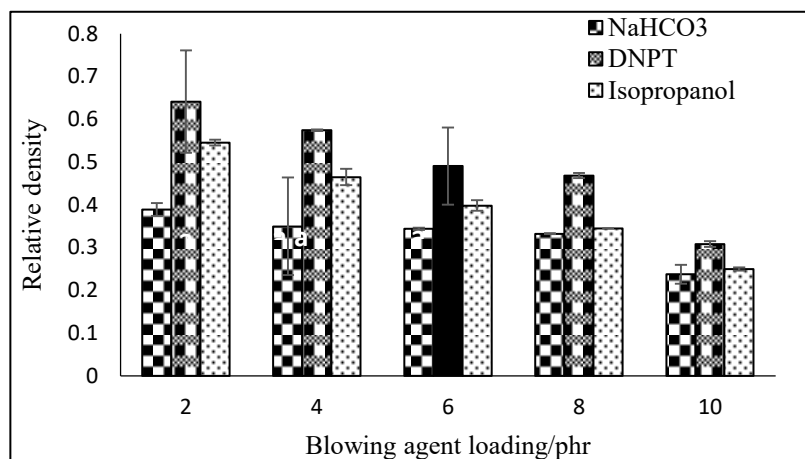


Fig. 5. Relative density of cellular rubber compounds

Crosslinking density

Crosslink density has decreased with increasing BA loading as indicated in Figure 6. DNPT incorporated cellular compound has a higher crosslinking density than the NaHCO₃ and isopropanol. This trend can be observed due to the fact that crosslinking and decomposition occur simultaneously; at high BA loadings; thus, the gas phase will be more prominent than the solid phase. As a result of that, thinner cell walls are formed, and consequently, less crosslinking occurs. It would be expected that similar crosslink densities would be obtained for all the samples because the same amount of sulphur (crosslinking agent) was used.

However, the NaHCO₃ used in this study decomposed endothermically (Wason *et al.*, 1992); this may result in crosslinking deficiency than DNPT as the BA loading increases. DNPT

decomposed exothermically (Nitzsche, 2003) and as a result it has higher crosslink density than NaHCO₃. At high loadings of NaHCO₃, more heat was absorbed from the system for the decomposition process hence, interrupting the crosslinking process. When considering DNPT, when the BA concentration is increased, more heat has been generated from the system making the crosslink formation process easier and as a result more crosslinks have been generated than NaHCO₃. Najib, *et al.* (2009) and Ariff, *et al.* (2008) has reported similar observations. Additionally, since the number of cells of N₂ generating BA is high (Di Maio *et al.*, 2005), the amount of rubber phase present to form the crosslinks is also high, indicating high results for cross link density for the compounds with DNPTBA.

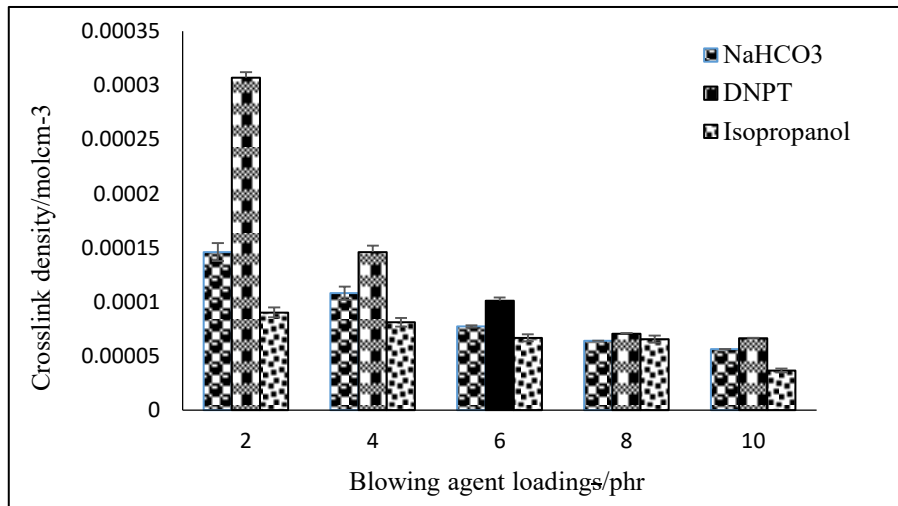


Fig. 6. Crosslinking density of cellular rubber compounds

Morphology analysis

Figures 7 (A), (C) and (E) which are produced using NaHCO₃ show open cell structure distinctly and other images that are produced using DNPT and isopropanol show closed-cell structures. When considering the organic BAs (DNPT and isopropanol) the morphology clearly indicates that it not only contains closed cells but also open cells are present in the structure to a certain extent. This indicates that even though DNPT and isopropanol BAs are known as closed-cell BAs, it generates open cells to a certain extent. Cellular rubber compounds at 10 phr of BA loading exhibit the fractures between bubbles due to high amount of gas produced from the thermal decomposition of NaHCO₃, DNPT and

isopropanol (inserted circle in Fig. 7). There is no uniformity in cell size when increasing the BA loading. Tangboriboon *et al.* (2015) and Charoeythornkhajhornchai, *et al.* (2016) have reported that cell size fluctuates when BA loading is increased. Ramesh, *et al.* (1991) stated that the size of the cell depends on the particle size of the BA and other chemical substances within the vulcanization process, temperature, pressure, and shear rate. Therefore, this can be the reason for the ununiformed cell structure in Fig.7. Furthermore, when considering Fig 7. (C), (E) it can be seen that as the BA loading increased certain level of agglomeration of particles are present (Wu & Shih, 1993).

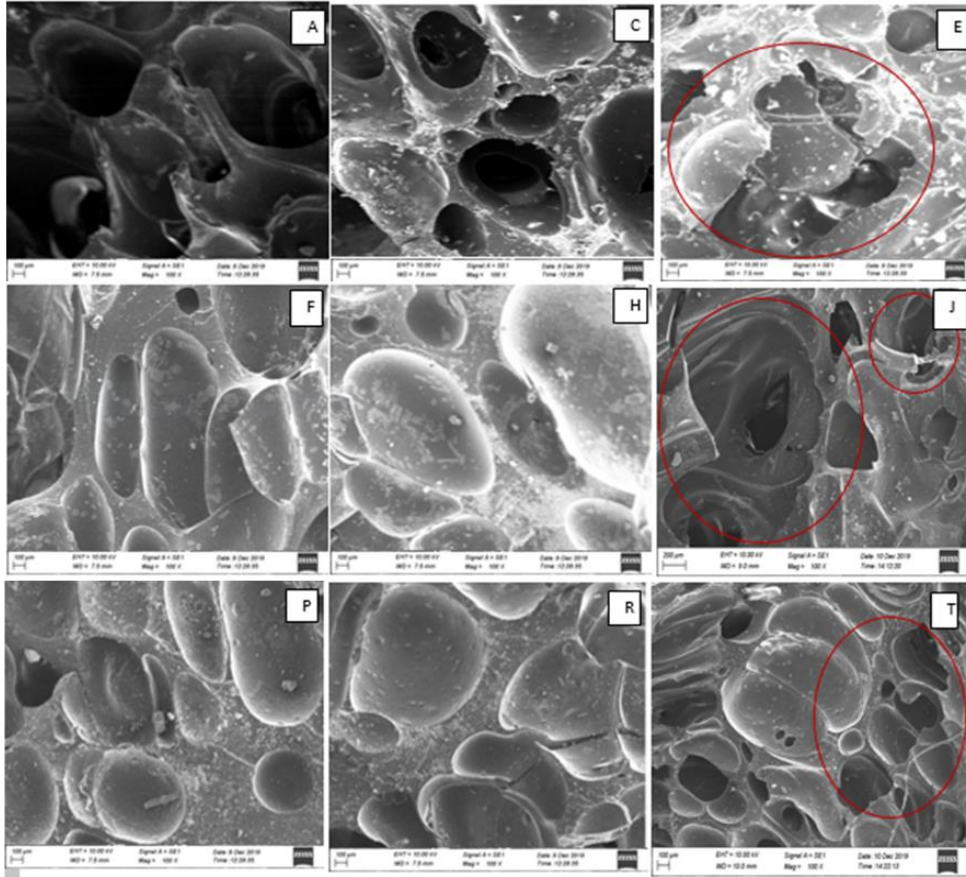


Fig. 7. SEM images of cellular rubber compounds **A.** NaHCO_3 -2 phr; **C.** NaHCO_3 -6phr; **E.** NaHCO_3 -10 phr; **F.** Isopropanol-2 phr; **H.** Isopropanol-6 phr; **J.** Isopropanol-10 phr; **P.** DNPT -2 phr; **R.** DNPT -6 phr; **T.** DNPT -10 phr

Water absorption

Fig. 8 illustrates an increasing trend of water absorption towards increasing BA loadings. This could be related to the relative density results. Najib, *et al.* (2009) reported that a decrease in relative density increases the number of cells per unit volume. As per Fig 5, the relative density is decreasing with the increase of BA loadings for each type of BA. Therefore the number of cells per

unit volume and free volume increases with the increase of BA loading (Najib *et al.*, 2009). As a result, water absorption is increasing with increasing BA loading. When considering the type of BA, NaHCO_3 shows a significantly high water absorption value than the DNPT and isopropanol. This can be attributed to the open/closed cellular nature of the resultant foam.

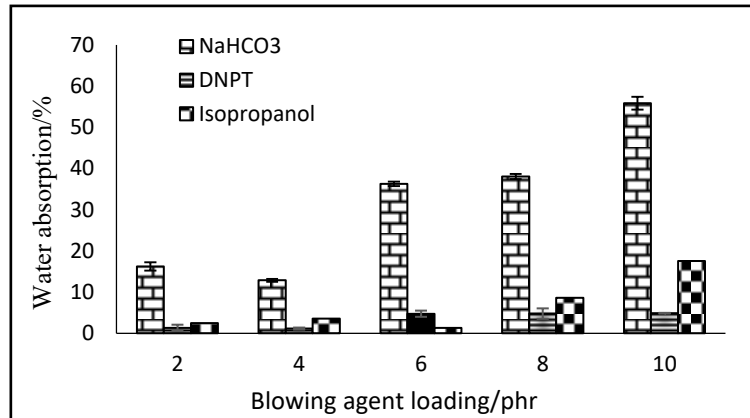


Fig. 8. Water absorption of cellular rubber compounds

Open-cell structures can absorb more water than closed-cell structures. Therefore, NaHCO₃ incorporated cellular compound has higher water absorption values than DNPT and isopropanol. When comparing the DNPT and isopropanol results DNPT has a higher relative density than isopropanol. Therefore, the number of cells per unit volume is higher in DNPT than in isopropanol. As a result of that, although both have closed cell structures, DNPT has the lowest water absorption value.

Conclusions

The increase in BA from 2 phr to 10 phr has led the microstructure of the cellular natural rubber changed from dense to porous phase. The highest porosity at 10 phr loading showed the lowest relative density. Further, the water absorption results at 10 phr shows the different abilities to absorb water for open and closed cell structures generated by NaHCO₃ and DNPT respectively

whereas the trend of DNPT levels from 6 phr have not generated a significant increment of water uptake. Furthermore, the mechanical properties of compounds were decreased when increasing the BA loadings. Therefore, lower loadings of BAs would generate better performance of cellular compounds in terms of tensile and elongation properties. Additionally, the selected control sample provided moderate results within the physical properties when compared to other compounds.

In addition, Isopropanol incorporated compound has the lowest compression set properties and hence, it could be used to produce soft sponge for makeup activities and cushion applications. Water absorption was increased when increasing NaHCO₃ loadings. Therefore, it can be recommended to produce rubber sponges for cleaning and washing proposes with the use of NaHCO₃. Compound prepared with DNPT showed superior mechanical properties hence, it would be better to

produce soft sponge rubber for shoe inner sole and shoe pads for high heels using DNPT.

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