# Effect of Blowing Agent Concentration on Cell Morphology and Impact Properties of Natural Rubber Foam

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**Abstract:** *The concentration of sodium bicarbonate as a chemical blowing agent was varied to evaluate its effect on the morphology and impact properties of natural rubber foam. The expandable rubber samples were prepared using a conventional two-roll mill and were then expanded via a heat transfer foaming process using compression moulding and an air-circulating oven. The physical properties of the natural rubber foams were characterised, and the results were observed to systematically correlate with the impact properties of the foam. The absorbed energy of the foam increases with decreasing crosslink density and relative foam density, which is associated with the formation of smaller foam cells and an increase in the number of cells per unit volume.*

**Keywords:** natural rubber, foam, morphology, impact

**Abstrak:** *Kandungan sodium bikarbonat sebagai agen pembusaan kimia dipelbagaikan bagi mengkaji kesannya terhadap morfologi dan sifat hentaman busa getah asli. Getah boleh-kembang disediakan menggunakan penggiling bergulung dua dan kemudian dibusakan menerusi proses pindahan haba menggunakan pengacuanan mampatan dan oven aliran udara panas. Sifat-sifat fizikal busa getah asli dicirikan dan keputusannya boleh dikaitkan secara sistematik dengan sifat hentaman busa. Tenaga penyerapan busa meningkat dengan penurunan ketumpatan sambung silang dan ketumpatan relatif busa, dimana ini memberikan purata saiz sel yang kecil dan peningkatan dalam bilangan sel per unit isipadu.*

**Kata kunci:** getah asli, busa, morfologi, hentaman

## 1. INTRODUCTION

Polymeric foam is important in various applications, due to its unique structural properties, such as its low weight, buoyancy, cushioning performance, impact damping, effective packaging, thermal and acoustic insulator properties, moderate energy absorption, and low cost.[1–5] The containment of the gas phase within the polymeric cell walls provides excellent properties for applications that involve impact. This is due to the fact that gas has excellent energy-absorbing

characteristics as compared to solid polymeric materials. Impact tests were conducted using an instrumented falling-weight impact tester. By continuously measuring the signal throughout the test, information regarding forces, displacement, deflection, and absorbed energy can be obtained. In addition, the introduction of a transducer has provided the possibility of analysing the impact properties of the foam.[6] Natural rubber was chosen due its natural availability and its renewable properties, in order to promote greater usage and thus eliminate the use of synthetic polymers, such as polyurethane. Most rubber foam applications have resulted from the desire to combine its low relative density with various other physical properties.[7] The foam structure can be controlled by the proper selection of blowing agents and curatives to achieve the correct balance between the gas generated and the degree of curing.[8–9] Sodium bicarbonate, which was used in this study, is an inorganic chemical blowing agent that releases carbon dioxide gas during decomposition. It decomposes at a relatively low temperature (145°C–150°C) and often results in an open-cell structure, which is suitable for use with natural rubber.[10–11] Although polymeric foam is widely used, studies concerning dry rubber foam have not received much attention, since most studies focus more on rubber foam derived from latex and synthetic polymers.[7] In this study, natural rubber foams were prepared by varying the concentration of sodium bicarbonate (4, 8, 10, and 12 phr), which was used as a blowing agent, at a fixed processing time and temperature. The influence of the sodium bicarbonate concentration on the physical and impact properties of the foams was analysed. The physical properties include the cure characteristics, relative density, crosslink density, number of cells per unit volume, average cell size, and morphology.

## 2. EXPERIMENTAL

### 2.1 Materials and Formulation

The natural rubber used in this study was SMR-L, obtained locally and having the standard specifications given by the Malaysian Rubber Board. Sodium bicarbonate was used as the blowing agent and was purchased from Merck. All other rubber ingredients, such as sulphur, zinc oxide, stearic acid, tetramethyl thiuram disulphide (TMTD), and benzothiazyl-2-cyclohexyl-sulphenamide (CBS), were of industrial grade. Compounding was carried out using a two-roll mill, according to the formulation shown in Table 1.

Table 1: Formulation of natural rubber compounds.

| Ingredient (phr)* | |
|---|---|
| SMR-L | 100 |
| Zinc Oxide | 4.0 |
| Stearic Acid | 2.0 |
| Tetramethyl Thiuram Disulphide (TMTD) | 2.5 |
| Benzothiazyl-2-cyclohexyl-sulphenamide (CBS) | 1.0 |
| Sulphur | 0.5 |
| Sodium Bicarbonate | 4 / 8 / 10 / 12 |

*Part per hundred of rubber

## 2.2 Cure Characteristics

Cure characteristics were evaluated using a Mosanto Rheometer (MDR 2000) according to ASTM D224 at a temperature of 150$^{o}$C for 30 min. The samples were first pre-vulcanised in an air-circulating oven for 2 min at a temperature of 100$^{o}$C, due to the implementation of a heat transfer foaming process, before being transferred into the rheometer.

## 2.3 Vulcanisation and Foam Process

The compounds were vulcanised and foamed via a heat transfer process. This process involved pre-vulcanisation using compression moulding at a temperature of 100$^{o}$C for 2 min, followed by simultaneous curing and foaming in an air-circulating oven for 20 min at a temperature of 150$^{o}$C.

## 2.4 Physical Properties

### 2.4.1 Relative foam density

The relative foam density was measured according to ASTM D3575, using Equation (1) as given below:

$$Relative\ Density = \frac{Foam\ Density}{Solid\ Density} \quad (1)$$

### 2.4.2 Crosslink density

The crosslink density was determined at room temperature according to ASTM D471. Different shapes of the vulcanised test piece were cut, and the original weight was measured using an analytical balance. Then, the samples were immersed in a glass vessel containing toluene for 6 h. 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 [Eqn. (2)] as follows: [12–13]

$$-\{\ln(1 - V_r) + V_r + \chi V_r^2\} = \rho V_0 M_c^{-1} V_r^{1/3} \quad (2)$$

where,

$\chi$ = Interaction constant characteristic between rubber and toluene, 0.42

$\rho$ = Rubber density

$V_o$ = Molar volume of toluene

$V_r$ = Volume fraction of rubber in swollen sample

$M_c$ = Average molecular weight between crosslinks

The volume fraction of rubber in the swollen sample, $V_r$ is given by Equation (3):

$$V_r = \frac{(X_r / \rho_r)}{(X_r / \rho_r) + (X_S / \rho_S)} \quad (3)$$

where,

$\rho_s$ = density of toluene, $\rho_r$ = density of the raw rubber, $X_s$ = mass fraction of toluene, which can be obtained from Equation (4), and $X_r$ = weight of the rubber, given by Equation (5).

$$X_s = \frac{(Weight\ of\ Swollen\ Sample - Original\ Weight)}{Weight\ of\ Swollen\ Sample} \quad (4)$$

$$X_r = 1 - X_s \quad (5)$$

Therefore, the obtained value of $M_c$ can be used to calculate the physical crosslink density, using Equation (6): [13–14]

$$[X]_{phys} = \frac{1}{2M_c} \tag{6}$$

### 2.4.3 Number of cells per unit volume

The number of cells per unit volume, the cell density, of the vulcanised sample at maximum expansion was calculated using Equation (7).[11]

$$N = \frac{6}{\pi d^3}\left(\frac{\rho_{rubber}}{\rho_{foam}} - 1\right) \tag{7}$$

where,
$N$ = number of cells per unit volume, $d$ = average cell diameter, $\rho_{rubber}$ = density of the solid rubber, and $\rho_{foam}$ = density of the rubber foam.

### 2.4.4 Morphology

A micrograph of the sample surface was obtained using a digital scanner. The surface was razor-cut perpendicular to its foaming direction. Then, the micrographs were analysed using Image Pro Plus Software to determine the average size of the foam cells. The average cell sizes of the samples were determined from measurements of 30 different cells in the obtained micrograph.

## 2.5 Impact Properties

Impact tests were conducted using a customised instrumented falling-weight impact tester. Samples with dimensions of 30 x 30 x 15 mm were placed at the centre of the testing plate. A constant-weight rectangular headstock was used, and the height was set to 600 mm; the rectangular headstock was placed to strike the centre of the sample in the foam rise direction. The impact tester includes a 12-bit PC acquisition data card and specifically designed software. The obtained data can be used to calculate the velocity, kinetic energy, and the absorbed energy, using the following equations:

$$v = \frac{x}{t} \tag{8}$$

where $v$, $x$, and $t$ are the velocity, distance between the optical sensors, and time, respectively.

The kinetic energy is given by Equation (9), with *m* and *v* as the mass and velocity, respectively:

$$E_k = \frac{1}{2}mv^2 \tag{9}$$

With the obtained value of kinetic energy, the absorbed energy can be calculated using Equation (10):

$$E_{abs} = E_k - E_{trans} \tag{10}$$

where $E_{abs}$ is the energy absorbed and $E_{trans}$ is the energy recorded by the transducer.

The impact toughness of the foam was obtained by dividing $E_{trans}$ by the sample volume, and the toughness is reported in units of J $mm^{-3}$.

## 3. RESULTS AND DISCUSSION

### 3.1 Cure Characteristics

The cure characteristics of natural rubber foam produced at 150°C with different blowing agent concentrations are shown in Table 2. The minimum torque ($M_L$) indicates the measurement of the stiffness of the unvulcanised rubber at the lowest point of the cure curve.[7] The results indicate that the blowing agent concentration did not affect the compound viscosity prior to crosslinking. It can also be seen that as the blowing agent concentration increased, the value of the maximum torque ($M_H$) decreased. $M_H$ represents the value of stiffness or the shear modulus of the fully vulcanised rubber and also indicates the crosslink density of the rubber.[1] The decrease in the $M_H$ value results from the fact that higher blowing agent concentrations generate more carbon dioxide gas in the rubber phase, simultaneously producing more microvoids. These microvoids reduce the shearing force; therefore, the torque began to decrease at the onset of the blowing agent decomposition and reached an equilibrium state.[15] The scorch time ($t_2$) is the induction time experienced by a rubber compound before vulcanisation initiates. Table 2 illustrates a decreasing trend in scorch time as the blowing agent concentration increases. This may be attributed to the decrease in compound viscosity. A decrease in the cure time ($t_{90}$) was also observed. Strauss and D'Souza[16] claimed that carbon dioxide gas can act as an efficient solvent in most polymers; the gas molecules accumulate interstitially between the polymer chains, thus increasing the free volume and mobility of the chain.

Table 2: Cure characteristics of natural rubber foam.

| Blowing Agent Concentration (phr) | 4 | 8 | 10 | 12 |
|---|---|---|---|---|
| Scorch Time, $t_2$ (min) | 3.15 | 2.93 | 2.85 | 2.80 |
| Curing Time, $t_{90}$ (min) | 5.99 | 5.72 | 5.49 | 5.50 |
| Minimum Torque, $M_L$ (dNm) | 0.15 | 0.11 | 0.15 | 0.14 |
| Maximum Torque, $M_H$ (dNm) | 6.65 | 6.30 | 6.23 | 6.09 |

### 3.2 Crosslink Density and Relative Density

Figure 1 illustrates the effect of the blowing agent concentration on the relative density and crosslink density of natural rubber foam. As greater concentrations of blowing agent were used, more gas was subsequently generated, reducing the relative foam density. Zakaria[15] reported that higher blowing agent concentrations 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. The crosslink density also slightly decreased with increasing blowing agent concentration. This is due to the fact that crosslinking and decomposition occur simultaneously; at high blowing agent concentrations, more carbon dioxide gas is present; thus, the gas phase will be more prominent than the solid phase. Hence, 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 sodium bicarbonate used in this study decomposed endothermically; this may result in crosslinking deficiency as the blowing agent concentration increases. At high concentrations of sodium bicarbonate, more heat was absorbed from the system, hence, interrupting the crosslinking process.[11] Furthermore, Sombatsompop and Lertkamolsin[7] suggested in his study that changes in the crosslink density of the foam may be caused by the destruction of crosslinks by the expansion of the gas during the decomposition of the blowing agent.

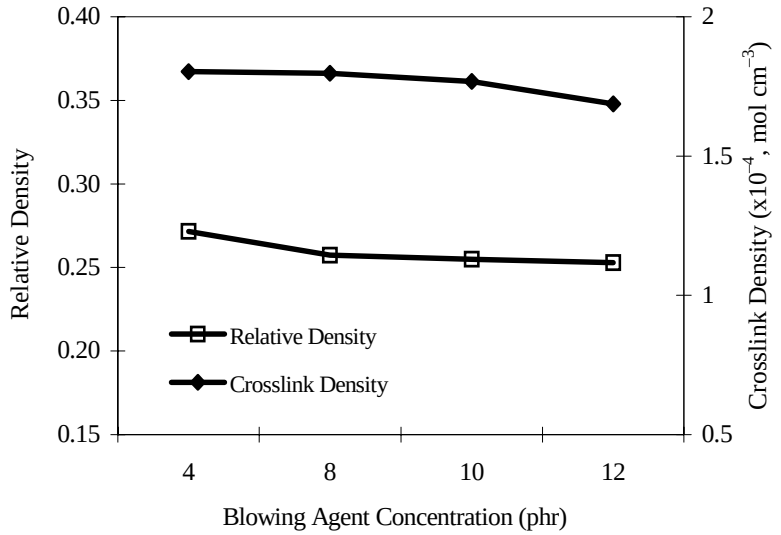


Figure 1: Effect of blowing agent concentration on relative density and crosslink density.

### 3.3 Average Cell Size

The decrease in relative density also played a role by increasing the number of cells per unit volume. Figure 2 shows that as the blowing agent concentration increased, the number of cells per unit volume also increased. The relationship between the average cell size and the blowing agent concentration is illustrated in Figure 3. It is found that the average cell size slightly decreased with increasing blowing agent concentration. The micrograph analysis (Fig. 4) shows that there is a systematic correlation between the number of cells per unit volume and the average cell size. An increase in the blowing agent concentration resulted in smaller, finer, and more uniform cells. The decomposition of high concentrations of carbon dioxide gas occurs simultaneously for a given time; thus, more cells formed at that same time. Consequently, the number of cells per unit volume increased, resulting in a smaller average cell size in the foam.

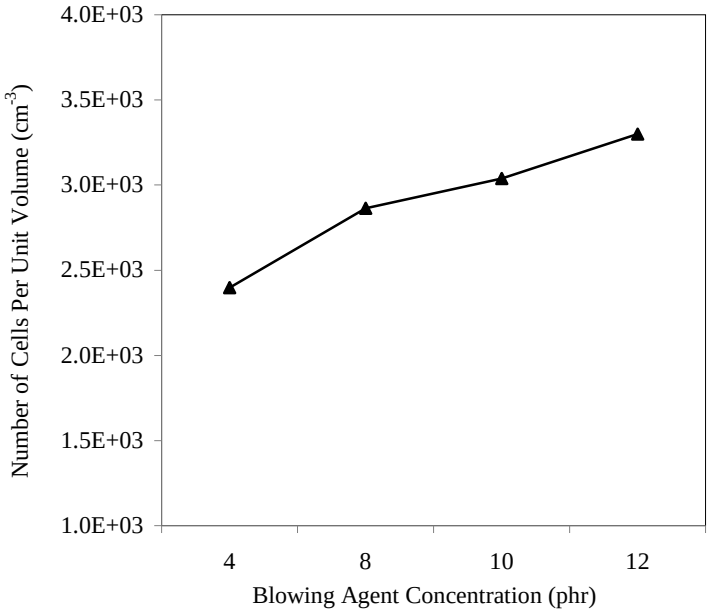


Figure 2: Effect of blowing agent concentration on number of cells per unit volume.

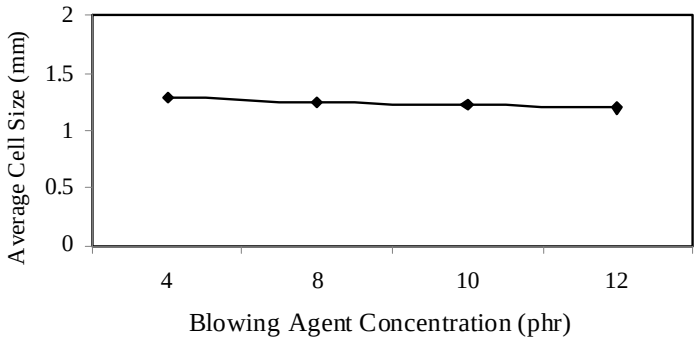


Figure 3: Effect of blowing agent concentration on average cell size.

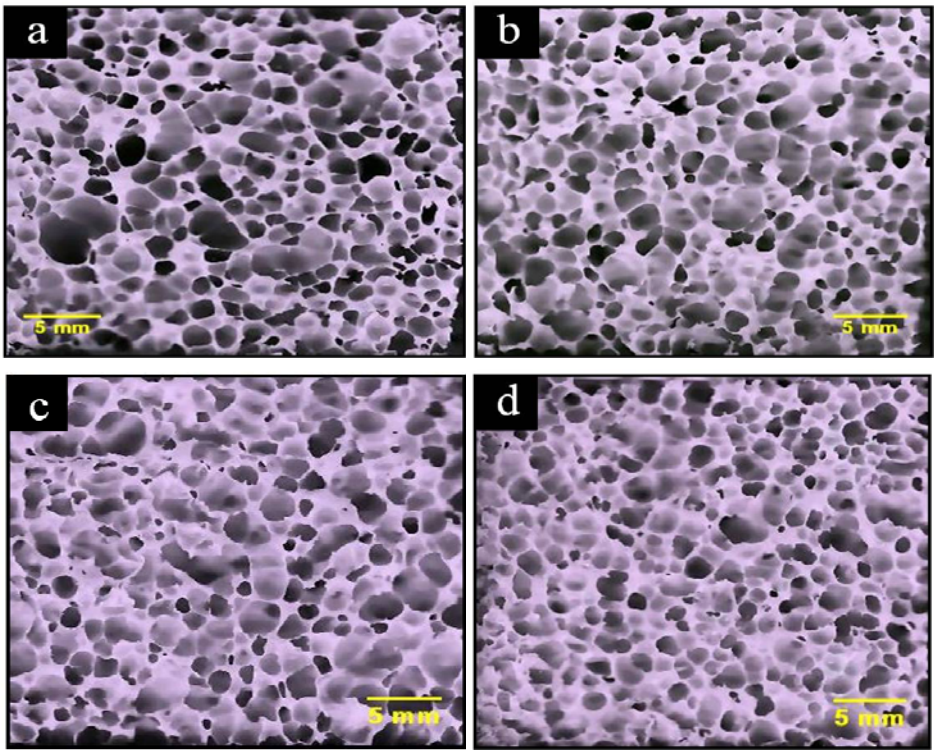


Figure 4: Micrographs of natural rubber foam at different blowing agent concentrations. (a) 4 phr; (b) 8 phr; (c) 10 phr; and (d) 12 phr.

### 3.4 Impact Properties

The relationship between the force and the displacement at different blowing agent concentrations, obtained from impact testing, is presented in Figure 5. The highest force was recorded for foam with a blowing agent concentration of 4 phr. From these data, the energy absorbed can be calculated and is tabulated in Table 3. The results reveal that the foams produced with higher blowing agent concentrations absorbed more energy. As discussed earlier, higher blowing agent concentrations resulted in lower foam relative densities, since more gas was generated. The unique properties of foam are due to the presence of the gas phase, which has excellent energy-absorbing characteristics. As more of the gas phase is present, the foam becomes softer. Wang[4] reported that the higher energy absorption of the lower relative density foams is a result of the larger deformation, the bending and buckling of the cell walls and edges.[3] The differences in the absorbed energy values in this study were very small; this may

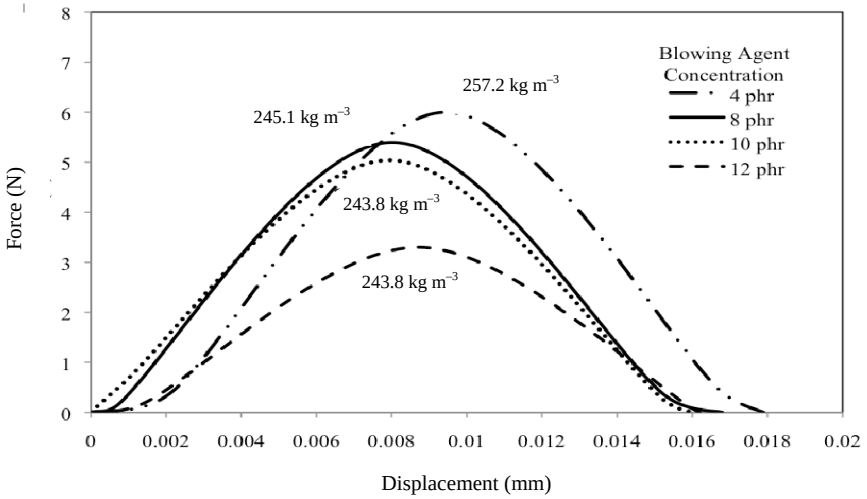


Figure 5: Relationship between force and displacement at different blowing agent concentrations.

Table 3: Effect of blowing agent concentration on the absorbed energy and toughness.

| Blowing Agent Concentration (phr) | Energy Absorbed (%) | Toughness (J $mm^{-2}$ x $10^{-5}$) | Foam Density (kg $m^{-3}$) |
|---|---|---|---|
| 4 | 99.85 | 4.43 | 257.2 |
| 8 | 99.88 | 3.57 | 245.1 |
| 10 | 99.89 | 3.28 | 243.8 |
| 12 | 99.94 | 2.04 | 239.5 |

be due to the presence of a bimodal structure. A bimodal structure is represented by the existence of large cells interspersed among many smaller cells.[2] When there is one large cell present, the properties of the foam will be lost. Since larger cells have thinner cell walls, when an impact force is applied, the cell wall is more likely to collapse and rupture.

## 4. CONCLUSION

In this study, different blowing agent concentrations (4, 8, 10, and 12 phr) were shown to influence the cell morphology of natural rubber foam, thus simultaneously affecting the impact properties of the foam. As the blowing agent concentration increases, more carbon dioxide gas decomposes, resulting in a smaller average cell size and increasing the number of cells per unit volume. This

simultaneously causes a decrease in the relative foam density and slightly decreases the crosslink density, thus reducing the ability of the foam to absorb the impact energy.

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