

Effect of Foaming Temperature and Rubber Grades on Properties of Natural Rubber Foams

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ABSTRACT: Foaming temperature and grade of dry natural rubber were varied to evaluate their effects on the morphology and mechanical properties of natural rubber (NR) foams. Three different grades of NR were used; namely ENR-25, SMR-L, and SMR-10. NR foams from these grades were produced at three different foaming temperatures, i.e. 140, 150, and 160°C. The study was carried out using formulated compositions containing sodium bicarbonate as the chemical blowing agent and were expanded using conventional compression molding technique via a heat transfer foaming process. The NR foams were characterized with respect to their relative foam density, density of crosslinking, cell size, compression stress, and compression set. Increase in foaming temperature resulted in lower relative density and larger cell size.

It was also discovered that the crosslink density slightly decrease with increasing foaming temperature. For mechanical properties, the highest foam density resulted in the highest compression stress. Compression stress at 50% strain increased with increasing foaming temperature and ENR-25 foam has the highest compression stress among the produced foams. The results showed that the morphology, physical, and mechanical properties of the rubber foams can be controlled closely by the foaming temperature and rubber grades. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2531–2538, 2008

Key words: rubber; density; crosslinking; swelling; morphology

INTRODUCTION

Rubber foam also known as cured expanded rubber in many applications which can be broadly classified into three major areas of thermal insulation, energy absorption, and structural uses.¹ Rubber foam or cellular rubber can be produced with either open or closed cell structures. Commercially available rubber-based polymeric foams are produced from synthetic polymers or rubbers such as acrylic, polyurethane (PU), ethylene vinyl acetate (EVA) copolymer, ethylene propylene diene (EPDM) terpolymer, and acrylonitrile butadiene rubber (NBR). As for natural rubber (NR), the most common and traditional way to manufacture foams is through the utilization NR latex which is in liquid form. The colloidal nature of the latex requires chemical stabilization (usually obtained through addition of ammonia) and this stabilization mechanism as well as the quality of the latex can be affected by storage time and environment.^{2,3}

Alternatively, rubber foams can also be produced using the solid form of NR or often called dry NR.

The processing of rubber foam from dry rubber involved compounding rubber with vulcanizing agents and blowing agent. The compounded rubber will be cured and simultaneously foamed at different temperatures to produce foams with range of end properties. Dry rubber foaming can be implemented through two processes which are called single stage process and heat transfer process. The expansion of the compound for the single stage process occurs while opening the mold. While in the two-stage heat transfer process, the first stage is identical to the single stage process but using lower temperature. On opening of compression molding platen, the pre-expanded rubber compound is immediately transferred to a circulating hot air oven at a higher temperature.⁴

Temperature is one of the important processing parameters that could yield different foam properties. Generally, foam properties are governed by the density, cell morphology, and mechanical properties of the base polymer.⁵ Higher temperature will cause higher gas decomposition of the blowing agent thus giving higher foam cell expansion in rubber. Increasing the temperature can also resulted in increase molecular mobility and caused reduction in the overall crosslink density throughout the system which subsequently will influence other end properties of rubber foam.⁶

Another important factor affecting rubber foaming process is the blowing agent. There are various sys-

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tems of chemical blowing agents available in the market ranging from the simple and inexpensive sodium bicarbonate up to the complex azo-compounds. Typically, selection of blowing agent for a foaming process depends on the type of gas exerts from their decomposition. Sodium bicarbonate is an inorganic blowing agent which is able to release carbon dioxide during decomposition. Most of the open-cell foams were produced using compounds containing sodium bicarbonate as their blowing agent. Some manufacturer used a nitrogen-releasing blowing agent in conjunction with sodium bicarbonate in order to obtain certain desired properties. Rubber compound containing these blowing agents will expand when the gases are released. Sodium bicarbonate is likely to be the most interest compound in list for the production of gas-filled cellular plastics and elastomers. It decomposes sufficiently in 30 min at 145–150°C with a relatively low foaming activity. Gas formation proceeds more smoothly and consequently there is no danger of gases escaping rapidly from mold or that large cell and pores will be formed.⁶

There are limited literatures covering the feasibility of foaming NR using sodium bicarbonate in their original form; i.e. without producing blends or using enhanced blowing agent (e.g. azo or hydrazine compounds).^{1,7,8} In this work, besides the effect of different foaming temperatures, grades of NR on physical properties NR foams were also investigated. Standard Malaysian Rubber (SMR) is standard grades of naturally harvested cis-polyisoprene which can vary in grade based on impurities content. Whereas, ENR is a product of latex stage epoxidation of NR under controlled conditions which gives a chemically-modified form of NR, called epoxidized natural rubber (ENR). The study will focus on changes of physical properties which include morphology, relative foam density, crosslink density, and also mechanical properties with respect to variation in foaming temperature and rubber grades. All rubber foaming compound formulations prepared in this study contain sodium bicarbonate as the blowing agent.

EXPERIMENTAL

Ingredients and formulations

NR (SMR-L, SMR-10, and ENR-25) was obtained locally and are having standard specification specified by the Malaysia Rubber Board. These three different grades of rubber were used to investigate the effect of NR grades on the properties of rubber foam using sodium bicarbonate as the blowing agent. Compounding procedure was

carried out on a two roll mill and is tabulated in Table I.

Cure characteristic

Cure characteristic were evaluated using a Monsanto Rheometer (MDR 2000) according to ASTM D224. Each sample containing 4 g respective compound was tested at different temperatures (140, 150, and 160°C), curing time (t_{90}) was determined from the plotted rheograph of MDR 2000. As the heat transfer foaming process was implemented throughout the study, the cure characteristic evaluation need to be as close as possible to the actual process. Because of that fact, each sample needs to be heated for 10 min in an air-circulated oven which was set at 100 °C before charging into the rheometer.

Vulcanization and foaming process

Compression molding was used to implement the first stage of the heat transfer and the compression platen temperature was set at 100°C. The sample was precured on the compression molding platen for 10 min followed by curing and foaming in an air-circulated oven at different temperatures (140, 150, and 160°C) for predetermined time obtained from the cure characteristic evaluation.

Physical properties

Morphology

Morphology study was carried out using scanning electron microscope (SEM) instrument, model Zeiss Supra 35VP-25-58. The SEM micrographs were then analyzed using ImagePro Plus software to determine the cell size and cell wall thickness. The results of average cell size and cell wall thickness were determined from measurement at 25 different locations of the captured image.

TABLE I
Formulations in Part Per Hundred of Rubber (phr)

Ingredients	ENR-25 (phr)	SMR-L (phr)	SMR-10 (phr)
Rubber	100.0	100.0	100.0
Zinc oxide	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0
TMTD	2.5	2.5	2.5
Sodium bicarbonate	8.0	8.0	8.0
CBS	1.0	1.0	1.0
Sulphur	0.5	0.5	0.5

Relative foam density

Relative foam density was measured using equation in accordance with ASTM D3575-93 as follows:

$$\rho^* = \frac{\rho_f}{\rho_s} \tag{1}$$

where, ρ^* is relative foam density; ρ_f , rubber foam density; and ρ_s , rubber matrix density.

Crosslink density

Based on ASTM D471-98, cured test pieces of different shape were cut and weighed using an analytical balance and each test piece was immersed in a glass vessel containing toluene at room temperature. After 6 h in vessel, the samples were then removed from glass vessel and excess toluene removed. The weight of the swollen sample was determined immediately.

The crosslink density of samples was determined by using Flory–Rehner equation [eq. (2)] as given below:

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

where,

- χ = interaction constant characteristic between rubber and toluene (0.42),
- ρ = rubber density,
- V_o = molar volume of the toluene,
- V_r = volume fraction of rubber in swollen sample
- M_c = physical crosslink concentration.

As for V_r , the following equation is used,

$$V_r = \frac{(X_r/\rho_r)}{(X_r/\rho_r) + (X_s/\rho_r)} \tag{3}$$

where, ρ_s is toluene density, ρ_r equals to raw rubber density, X_s is mass fraction of toluene which can be obtained as follow;

$$X_s = \frac{(\text{Weight of swollen sample} - \text{Initial weight})}{\text{Weight of swollen sample}} \tag{4}$$

and X_r is weight of rubber which given as:

$$X_r = 1 - X_s \tag{5}$$

Physical crosslink density $[X]_{\text{phys}}$ can be obtained through calculation using the following equation which is a result of rearranging eq. (2);

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

Mechanical properties

Compression test

Compression load-deflection measurements were performed using the Instron universal testing machine fitted with a compression jig. Test specimens were deformed at cross head speed of 20 mm min⁻¹ and compressed up to 75% of their original thickness.

RESULTS AND DISCUSSION

Effect of different temperatures

Table II shows minimum torque for ENR-25 compound decreased when temperature is increased from 140 to 160°C. The decrease in minimum torque was due to increase in the temperature which resulted in lower viscosity. Meanwhile, the maximum torque also decrease when the increased foaming temperature. Increase of maximum torque is due to the presence of crosslink density that caused restriction to flow hence increasing the viscosity.⁹

Figure 1 shows that the cell of ENR-25 foam becomes more or less spherical shape with increasing temperature and cells diameter at 140°C are slightly more uniform in distribution compared with that of at 160°C. Obviously the result shows (Fig. 1) that the cell wall thickness decreased due to increasing temperature which subsequently resulted from amount of gas present in foam cell. The gas generated by blowing agent will promote the cell walls to expand further and eventually these walls will coalesce or may even rupture to form bigger cell. Typically, the mechanism of foaming rubber is similar to that of plastic foam.

TABLE II
Results of Cure Characteristic Evaluation

Cure characteristics	ENR-25			SMR-L			SMR-10		
	140°C	150°C	160°C	140°C	150°C	160°C	140°C	150°C	160°C
Curing time, t_{90} (min)	8.81	5.31	3.50	8.87	5.19	3.02	8.94	5.73	3.47
Minimum torque, M_L (dNm)	0.15	0.06	0.03	0.10	0.07	0.09	0.23	0.17	0.12
Maximum torque, M_H (dNm)	6.52	6.45	6.41	5.78	5.76	5.63	5.79	5.78	5.72

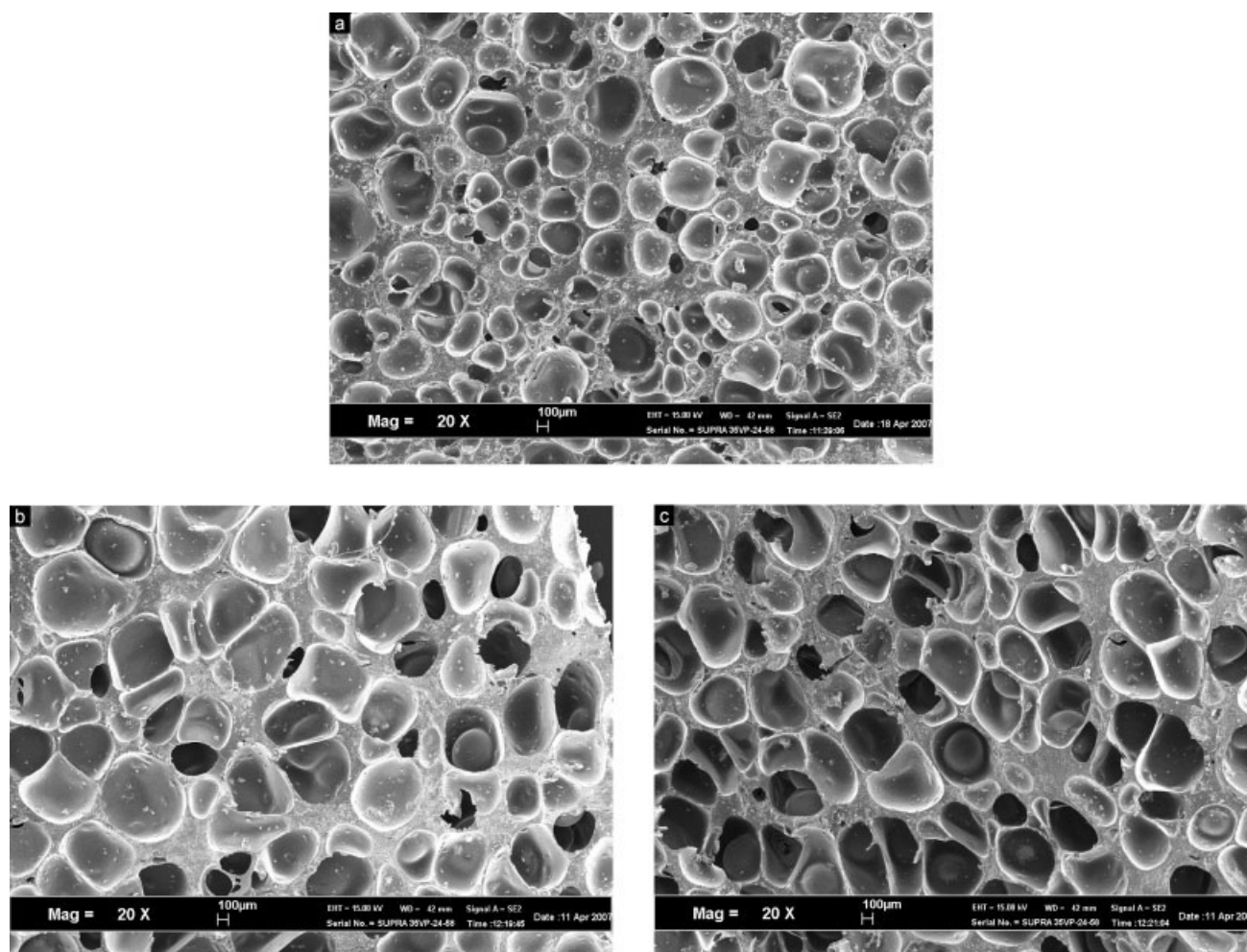


Figure 1 Morphology ENR-25 at different foaming temperatures (a) 140°C, (b) 150°C, and (c) 160°C.

Figure 2 reveals quantitatively that density of rubber foam decreased with increasing foaming temperature whereas the average cell size increased, which is in agreement with qualitative findings of Figure 1. It can be seen from Figure 2(b) that relative foam density displays similar trend to crosslink density with respect to increasing foaming temperature. Although there are slight changes in density as the temperature increases, there is not apparent decreasing or increasing trends for both parameters. This was projected to be due to the gradual foaming approach of heat transfers process and chemical nature of ENR which are likely to trigger the vulcanization process faster than the cell expansion process hence limiting windows of cell expansion.

Nevertheless, using results of minimum torque (Table II) and qualitatively evidence of Figure 1, it was obvious that less restriction to expansion was achieved at higher foaming temperature. In this condition, the existence of greater gas volume and lower crosslink density, will increase the cell size and subsequently decrease foam density. The peculiar

occurrence of decrease in crosslink density at higher temperature would be probably caused by the breakdown of strained crosslink in the polymer network.⁸

As for the effect of foaming temperature on mechanical properties, Figure 3 summarizes the result of compression stress–strain curves of ENR-25 foams. Typically, a compression stress–strain curve of polymeric foam would exhibit the existence of initial linear elastic region and the subsequent plateau stress region. The linear elastic region corresponds to cell edge bending of foam cell, whereas the plateau stress region relates to progressive cell collapse by elastic buckling of polymer matrix.¹⁰ However, compression stress–strain curves of ENR-25 foams expanded at different foaming temperatures did not significantly display the above features. The absence of these features was due to very small cell size of ENR foam cells and the fact that more polymer matrix occupying a specific area which is indicated by relatively high values (i.e. in the vicinity of 0.4) of relative foam density of ENR-25 shown in Figure 2(a). Furthermore, the use of relatively large

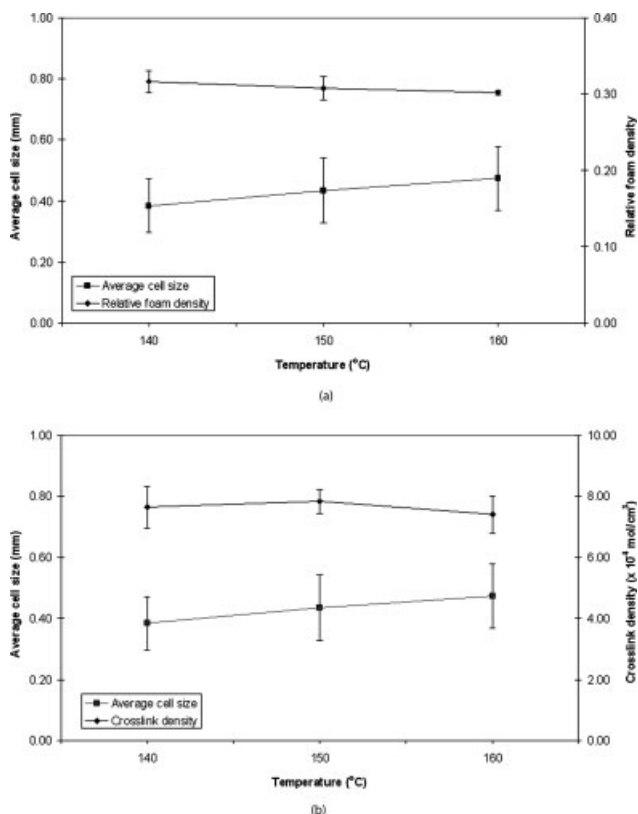


Figure 2 The effect of temperatures on (a) average cell size and relative foam density and (b) average cell size and crosslink density for ENR-25.

scale range of compression stress (i.e. *y*-axis) in Figure 3 would also suppress any changes occurred at low compression stress.

The existence smaller cells would cause shorter time requirement to collapse the cell walls resulting the plateau region to be not clearly visible in Figure 3. In addition, the presence of more highly crosslinked polymer matrix within an area would enhance the elastic characteristic of the foam cells hence exaggerating the elastic character that

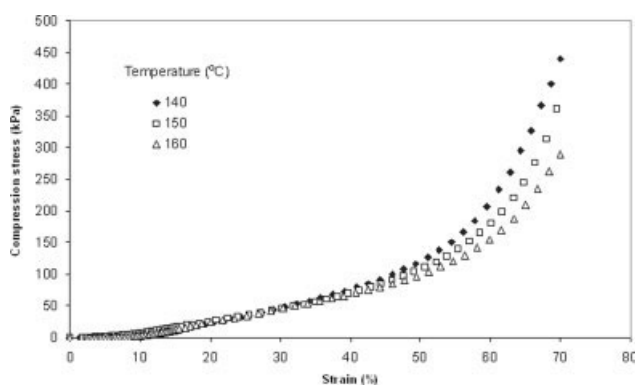


Figure 3 The compression stress-strain curves of ENR-25 foams at different foaming temperatures.

dominates the stress-strain curve. Therefore, to prove that linear elastic and cell collapse regions also exist in ENR-25 foam, smaller scale range of compression stress was used (presented in Fig. 4) to magnify changes in the compression stress-strain curve. Figure 4 is actually a refined version of Figure 3 which depicts significantly changes in stress-strain curve's slope at low compression stress, which will signify the linear elastic cell edge bending and plateau cell collapse regions. It was apparent that the initial region has higher slope value than the subsequent slightly plateau region. Figure 4 proved that ENR-25 foam also possess similar features of typical compression stress-strain curve of polymeric foam but can be only observed at low compression stress. Since ENR-25 foams produced in this study have relative foam densities values in the vicinity of 0.3 [refer Fig. 2(a)], this finding is in agreement with Gibson and Ashby,¹¹ who reported that compression stress-strain curve for elastomeric foams with relative density greater than 0.3 would only exhibit linear elasticity at very low stress or strain and display no real plateau in the subsequent region.

Referring back to Figure 3, it was also observed that the compression stress at 50% strain differ at different foaming temperatures showing that the compression stress at low temperature (140°C) is higher compared with that of at high temperature (160°C). The cell size increased with increasing foaming temperature and consequently causing decrease in the compression stress. Smaller cells will tend to have higher cell wall thickness (as tabulated in Table III) thus giving greater resistance to collapse and further on yielding greater compression stress compared with bigger cells with low cell wall thickness. At strain above 50%, densification and the bending of cell initiate and cell walls begin to contact each other and the stress starts to increase drastically.

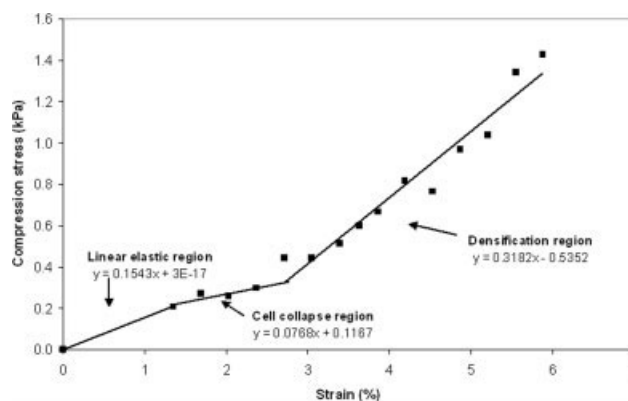


Figure 4 The existence of linear elastic and plateau stress regions at low compression stress for ENR-25 foam expanded at 140°C.

TABLE III
Effect of Foaming Temperature on Average Cell Wall
Thickness of ENR-25 Foam

Foaming temperature (°C)	Average cell wall thickness (μm)
140	128.0 ± 28.9
150	80.4 ± 28.7
160	54.2 ± 17.6

Effect of rubber at constant temperature

Figure 5 shows the morphology for different types of rubber foams produced at 150°C. At constant temperature, the cell size for SMR-L and SMR-10 foams are greater compared with that of ENR 25 foam. This subsequently indicates that greater expansion occurred in both of SMR compared with ENR-25. Figure 5 also shows that the cell wall thickness for ENR-25 is higher due to small cell size and higher crosslink gave greater restriction to expansion. The occurrence of such trend in cell size result can be linked with the amount crosslink density

available in each type of rubber which is displayed in Figure 6. Rubber with higher degree of crosslink density would provide stiffer cell walls hence giving higher restriction to expansion and in the case, would definitely refer to ENR 25 foam.

It was also noted that foams produced from different grades of SMR do not exhibit significant difference in both crosslink density and cell size. Both rubbers are similar in term of chemical structure, i.e. *cis*-1,4 polyisoprene and the only difference between SMR-L and SMR-10 is in the ash content where SMR-10 has higher (max. 0.75 wt %) ash content than SMR-L (max. 0.50 wt %).¹² Foaming rubbers having the same chemical nature would project similar extent of vulcanization mechanism and therefore yield more or less similar results of crosslink density and cell size. Whereas for ENR-25, it was estimated that the vulcanization process occurred more vigorously with the presence of epoxide groups on the NR main chain which could act as an added cross-linking sites in compliment with the carbon double bond.¹³ This can also be confirmed through the

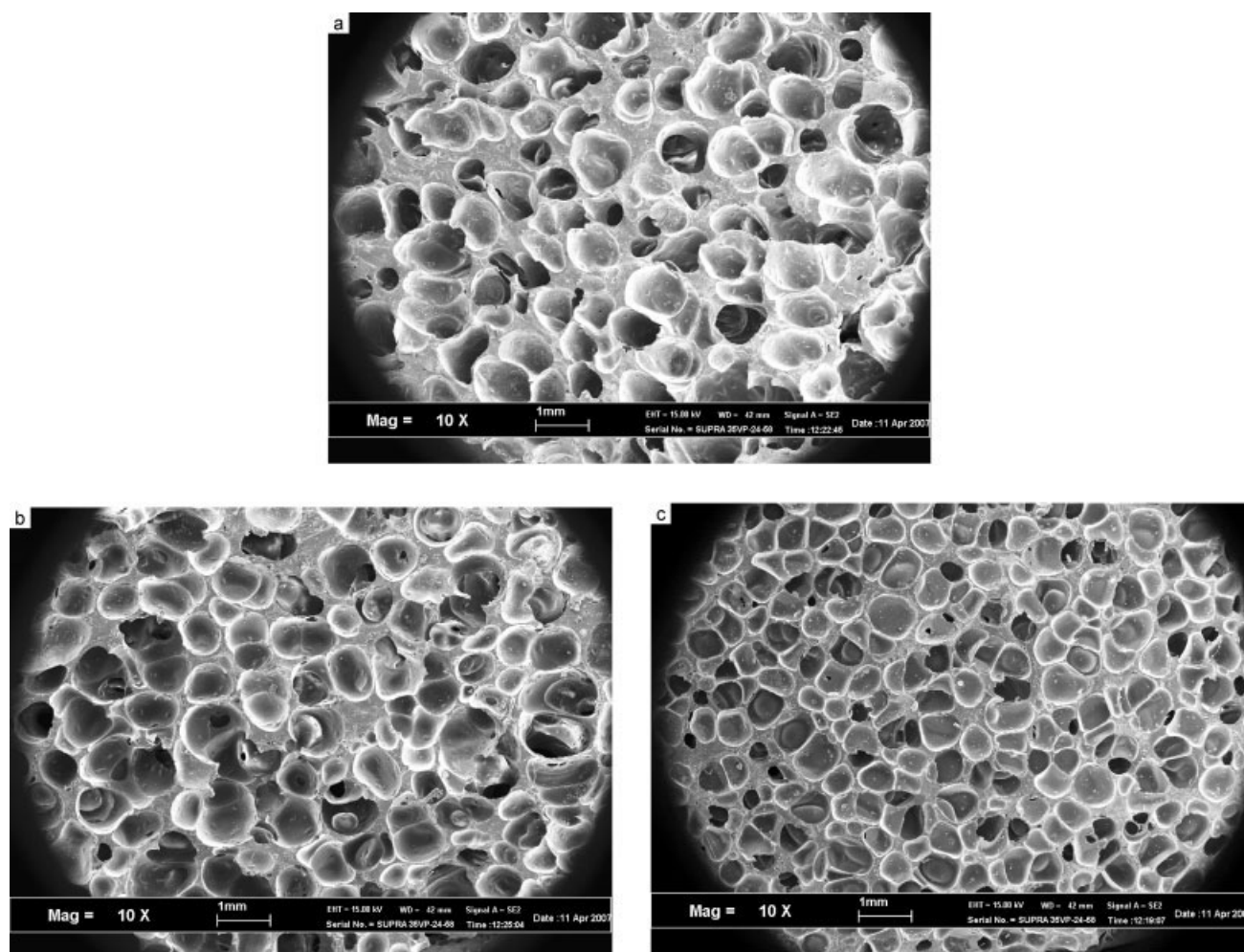


Figure 5 Morphology for (a) SMR-L, (b) SMR-10, and (c) ENR-25 foams at 150°C foaming temperature.

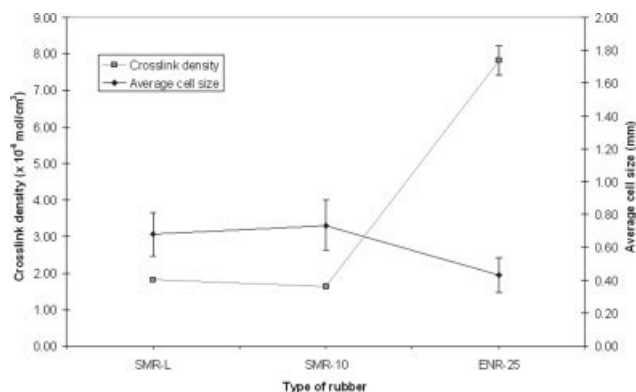


Figure 6 The effect of different grade of natural rubber foam properties on cell size and crosslink density at foaming temperature of 150°C.

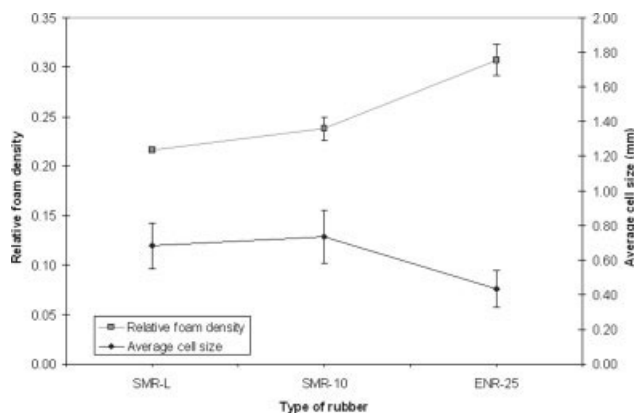


Figure 7 The effect of different grade of natural rubber foam properties on cell size and relative foam density at foaming temperature of 150°C.

higher maximum torque of ENR-25 (6.45 dNm at 150°C) compared with that of SMR-L (5.76 dNm) and SMR 10 (5.78 dNm) shown in Table II previously. All the results proved that ENR-25 possess higher crosslink density and therefore give greater resistance towards cells expansion hence giving smaller foam cell with thicker cell walls (refer Table IV).

Foams with smaller cell size tend to have higher density. The presence of thicker cell walls and more rubber matrix per unit area would be the cause of density increment. This is depicted in Figure 7 where ENR-25 foams display the highest relative foam density value. Here, the effect of base polymer density has been cancelled out by dividing the resultant foam density with base polymer density to give the relative foam density parameter.

It was discovered that more foam cells can be packed in a unit area (Fig. 5) for ENR-25 foams which projects more matrix walls present and therefore yield higher relative foam density compared with SMR-L and SMR-10.

It is known that the mechanical properties of cellular solids or foamed materials are highly dependent on their base material, cell structure, and density.¹⁰ Figure 8 shows the effect of rubber type (i.e base polymer) towards compressive stress–strain of NR foams. As described previously, regardless of their base polymer density, ENR-25 foam has the smallest cell size and the highest relative foam density among all the prepared NR foams. Therefore, it is obvious to see that ENR-25 foams have higher compression

stress compared with SMR-L and SMR-10 foams. This behavior give ENR-25 foams a better resistance to buckling and collapse of cell walls during the compression test. Consequently, the yield point and compression stress for ENR-25 foam at plateau regime is higher.

The plot shows that most of the foam samples (i.e. SMR-L and SMR-10 foams) start to buckle at 20% strain (plateau region) and then deform further to form an exponential curve shape approaching the end of the test. Both of SMR foams have long and apparent plateau region compared with ENR-25. This is because greater time is required in SMR foam cells to progressively collapse through elastic buckling as the consequence of their larger cells. It was also observed that the modulus and compression stress increase with increasing the foam density. Overall, the compression stress for ENR-25 is slightly greater compared both of SMR. This was due to the high degree of crosslinking occurred in ENR-25 foams as discussed previously which resulted in greater restriction to expansion, giving higher foam density and subsequently yield higher compression stress at 50% strain.

TABLE IV
Average Cell Wall Thickness of Natural Rubber Foams Produced from Different Grades of Rubber

Rubber grades	Average cell wall thickness (µm)
SMR-L	49.4 ± 10.9
SMR-10	65.1 ± 14.2
ENR-25	80.4 ± 28.7

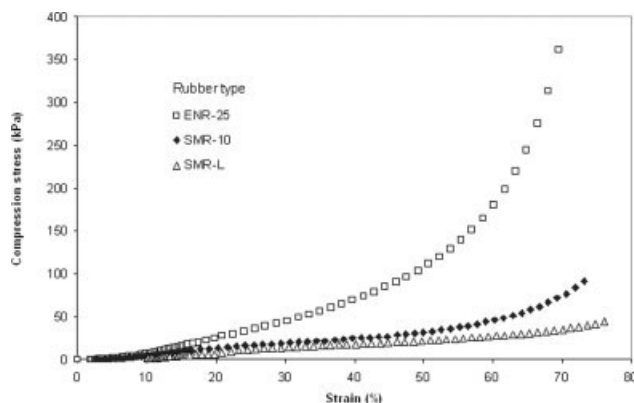


Figure 8 Compression stress–strain curves various types of natural rubber foams.

CONCLUSION

Increase in foaming temperature resulted in lower relative foam density and larger cell size. It was also found that the crosslink density slightly decreased with increasing the foaming temperature with respect to ENR-25 foams. For mechanical properties, the highest foam density resulted in the highest compression stress and compression stress at 50% strain decreased with increasing foaming temperature. ENR-25 has the highest compression stress at 50% strain compared with SMR-L and SMR-10 foams produced at constant foaming temperature.

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