

Preparation and characterization of natural rubber foams: Effects of foaming temperature and carbon black content

Eun-Kyoung Lee[†] and Sei-Young Choi

Department of Applied Chemistry, Cheongju University, Cheongju 360-764, Korea

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Abstract—The influence of the foaming temperature and carbon black content on the cure behavior and mechanical properties of natural rubber foams was investigated at five temperature zones by 5 °C interval and different feeding ratios of the carbon black. The physical properties of the foamed NRs were then measured as a function of the foaming temperature and carbon black content, respectively. The optimal temperature for vulcanization and foaming of NRs in this study was considered to be 165 °C where density of the foamed NR is lower than that at other four temperature zones. The thickness of each of the struts formed within the rubber matrix decreased with the increasing foaming temperature, while it increased with the increasing carbon black content, supporting the density characteristics. The tensile properties of the foamed NRs such as tensile strength, tear strength and modulus gradually increased with the increasing and carbon black content, while elongation at break decreased.

Key words: Vulcanization, Cure Behavior, Foaming, Cure Rate Index

INTRODUCTION

Cellular polymers may be prepared by a variety of methods. The most important process, by far, consists of expanding a fluid polymer phase to a low-density cellular state and then preserving this state [1,2]. This has been termed a foaming or expanding process. Other methods of producing a cellular state include leaching out solid materials which have been dispersed in a polymer, sintering small particles together, and dispersing small cellular particles in a polymer. The latter processes, however, are of minor importance and are relatively straightforward processing techniques [3-5].

The expansion process may be divided into three steps: creating small discontinuities or cells in a fluid or plastic phase, causing these cells to grow to a desired volume, and stabilizing this cellular structure by physical or chemical means.

Cellular polymers have been commercially accepted in a wide variety of applications since the 1940s because of advantages of light weight, buoyancy, cushioning performance, thermal and acoustic insulation, impact damping, and cost reduction. The high strength-to-weight ratio of wood, good insulating properties of cork and balsa, and cushioning properties of cork have contributed to the incentive as well as to the background knowledge necessary for the development of a broad range of cellular synthetic polymers in use today.

Most uses of rubber foam have been derived from the desired combination of low density and some other physical properties. Although foamed rubber is widely manufactured and is in service all over the world, the available articles concerning their electrical, mechanical and physicomechanical properties are few in number. In fact, the search for new materials with specific physical properties has been mainly empirical, because no exact theory is currently known that relates the macroscopic properties of multiphase composites to

their microscopic structure. The correlation between experimental data in both reinforced rubber and foamed rubber will be attractive from the experimental and theoretical point of view [6,7].

Foams can be reinforced by adding rigid fillers or short glass fibers to the polymer before it is foamed. The effects of reinforcing fillers such as carbon black, carbon fiber, and silicate, on the physical properties of rubber composites have been extensively studied experimentally and theoretically. The compounding technique and also the vulcanization condition were found to affect the final foam density. Foams are characterized by density, cell size, shape and the modulus of the base polymer [8].

To obtain optimal foam expansion and good physical properties of the foams, optimal crosslinking is the most critical requirement. In this study, the NR foams were prepared at various temperatures (145 °C, 150 °C, 155 °C, 160 °C and 165 °C) and different feeding ratio of the filler (15, 30, 50, 70 phr). The effect of the foaming temperature and reinforcing filler content on the cure behavior and mechanical properties of the foams was studied. Furthermore, the physical properties of the foams in terms of tensile strength, elongation at break, tear strength and modulus were investigated as a function of foaming temperature and reinforcing filler content. The density and expansion ratio of the foamed NRs were also studied, and a microscope was used to investigate the effects of the foaming temperature and filler content on the morphologies of the foamed NRs.

EXPERIMENTAL

1. Materials

The NR used was SMR obtained from Malaysia. All other rubber ingredients, such as sulfur, zinc oxide, stearic acid, paraffine oil, 2-Mercaptobenzothiazole (MBT) and mercapto benzothiazyl disulfide (MBTS) were of commercial grade. As a blowing agent and blowing activator, respectively, N,N'-dinitroso pentamethylene tetramine (DPT) and Cellex-A were received from Kumyang, Korea.

[†]To whom correspondence should be addressed.

E-mail: eklee@cju.ac.kr

Table 1. Formulations of the NR compounds

Ingredients (phr) ^a	Sample ^b			
	NF-1	NF-2	NF-3	NF-4
SMR-L		100		
St. acid		2.5		
ZnO		5.0		
Carbon black	15	30	50	70
P. oil		27.5		
MBTS		1.2		
MBT		0.1		
Sulfur		2.0		
DPT		10.4		
Cellex-A		4.2		

^aParts per hundred rubber.^bNF-1, 2, 3, and 4; N refers to NR, F foam and 1-4 filler content (15, 30, 50, 70, respectively).

2. Sponge Rubber Preparation and Formulation

NR compounds were prepared in four different combinations. NR was compounded by using a two-roll mill according to the recipe shown in Table 1. The ingredients were added in the same order as written in order in Table 1. The compounded blend was then passed endwise ten times through the mill at the 1 mm opening, after which it was sheeted off at 2 mm thick. The specification of the mill is as follows: length, 0.45 m; radius, 0.10 m, speed of slow roll, 20 rev min⁻¹ and gear ratio, 1.4. The compounded rubber was left for at least 24 h before vulcanization. The vulcanized samples were shelf aged for at least 48 h before testing. To investigate the effects of the foaming temperature and filler content on the physical properties and morphology of NR foam, the foaming was carried out at five temperatures (145–165 °C by 5 °C interval). The compounded NRs were then compression molded along the mill grain direction by using an electrically heated hydraulic press at different temperatures under a pressure of 14 kgf/cm² for their optimum cure time t₉₀. Efficient blowing agent (DPT) and blowing promoter (Cellex-A) were carefully selected by TGA analysis.

3. Cure Characteristics and Mechanical Properties

Cure characteristics were studied with a rheometer (MDR 2000E, Alpha Technologies) according to ASTM D 2240-93. The scorch time, cure time and cure rate index were calculated based on the rheometer curve or curing curve. Density of the foam was measured by a buoyancy method using a densimeter (SD-200L, MIRAE). 2×2 cm sample was cut out of a foam, and its thickness, t₁ (cm) and weight, W₂ (g) were measured and expansion ratio was calcu-

lated from the following equation [9].

$$\text{Expansion ratio} = [(2 \times 2 \times t_1) / W_2] \quad (1)$$

where t₁ is the thickness; W₂ the weight of the sample.

Tensile properties of the samples such as tensile strength, elongation at break, tear strength and 50% and 100% moduli were carried out using an Instron Universal Testing Machine (4444-C10283) at a cross-head speed of 50 mm/min and at 25±2 °C. The experimental conditions for the tear measurements were the same as those for the tensile testing. The morphology of the NR foams was analyzed by using a microscope (Hi Scope Advanced KH-3000). A thin slice cut vertically from the foamed NR was magnified with a microscope and its picture was taken.

RESULTS AND DISCUSSION

The results obtained in this study are discussed with respect to the cure properties, foaming characteristics and mechanical properties of the foamed natural rubbers.

1. Blowing Promoter and Cure Characteristics

The decomposition temperature of a mixture of DPT and Cellex-A was found lower than that of single DPT by TGA analysis. DPT-A refers to a mixture of DPT and Cellex-A. Decomposition temperature changed from 206 °C to 138 °C by the addition of blowing promoter, Cellex-A.

The cure characteristics of the foamed NRs with different carbon black contents are presented in Table 2. Scorch time, t_{s2}, or time to incipient cure is a measure of the time when the premature vulcanization of the material occurs. It is the time taken for the minimum torque value to increase by two units. It can be seen that scorch time decreases with increasing foaming temperature and filler loading. This observation may be attributed to the viscosity increase with the increasing carbon black content and prevulcanization along with the rising foaming temperature. Therefore, a shorter time is required for the beginning of the vulcanization process for the NR foam compounds. A decreasing trend of the cure time, t₉₀ was also observed upon increasing foaming temperature and carbon black content. The variation of minimum torque and maximum torque with increasing foaming temperature and carbon black content is also given in Table 2. A minimum torque, ML is a measure of stiffness of the unvulcanized test specimen taken at the lowest point of the cure curve. It can be seen that the minimum torque increases with increasing carbon black content but decreases slightly with increasing foaming temperature. The former is due to the viscosity increase and decrease of the relative amount of process oil with the

Table 2. Rheometric characteristics of the NR foams

Temp. (°C)	Scorch time, t _{s2}				Cure time, t ₉₀				Minimum torque, ML (dNm)				Maximum torque, MH (dNm)			
	NF1	NF2	NF3	NF4	NF1	NF2	NF3	NF4	NF1	NF2	NF3	NF4	NF1	NF2	NF3	NF4
145	2.34	2.28	2.08	1.90	5.73	5.63	4.98	4.45	0.16	0.37	0.53	1.01	7.5	10.1	12.1	14.7
150	1.76	1.72	1.57	1.45	3.90	3.88	3.72	3.71	0.11	0.32	0.46	0.90	7.3	9.7	11.9	14.5
155	1.30	1.27	1.16	1.05	2.98	2.87	2.86	2.74	0.13	0.30	0.45	0.87	7.2	9.3	11.7	14.3
160	1.04	0.98	0.91	0.84	2.04	2.02	1.95	1.88	0.05	0.20	0.30	0.66	6.5	8.6	10.8	13.8
165	1.81	0.81	0.72	0.65	1.65	1.61	1.48	1.32	0.04	0.19	0.29	0.63	6.2	8.1	10.3	13.7

Table 3. Curing characteristics and expanding properties of the NR foams

Temp. (°C)	Delta torque (dNm)				Cure rate index				Density (g/ml)				Expansion ratio			
	NF1	NF2	NF3	NF4	NF1	NF2	NF3	NF4	NF1	NF2	NF3	NF4	NF1	NF2	NF3	NF4
145	7.37	9.81	11.6	13.6	29.0	29.7	34.8	39.2	0.60	0.68	0.71	0.75	1.64	1.56	1.50	1.50
150	7.25	9.38	11.8	14.1	42.8	44.6	46.2	48.9	0.55	0.63	0.64	0.70	1.84	1.80	1.58	1.53
155	7.08	0.06	11.4	13.9	55.2	60.1	62.3	63.5	0.51	0.55	0.63	0.67	1.89	1.81	1.71	1.54
160	6.53	8.42	10.5	13.2	89.2	95.2	97.7	100	0.44	0.52	0.58	0.61	2.16	1.87	1.73	1.55
165	6.17	7.93	10.0	13.0	117	125	129	149	0.43	0.50	0.57	0.59	2.24	2.03	1.77	1.57

increasing carbon black content; the latter due to the viscosity decrease by the plastic deformation with increasing curing temperature. A maximum torque, MH is a measure of stiffness or shear modulus of the fully vulcanized test specimens at the vulcanization temperature. In other words, it is also a measure of crosslink density. Both the maximum torque and the difference, delta torque between the maximum and minimum torque increase by the formation of crosslinks between the macromolecular chains. The addition of more filler into NR matrix and relative decrease of the oil content are also other factors. They, however, decrease with increasing foaming temperature due to the decrease of the force applied to the rotating disk when the blowing efficiency of NR foam increases.

The cure rate index of the foamed NRs with various foaming temperatures and carbon black contents is presented in Table 3. The cure rate index is calculated as follows [10]:

$$\text{Cure rate index} = \frac{100}{(\text{cure time, } t_{90} - \text{scorch time, } t_s)} \quad (2)$$

Cure rate index at 145 °C is smaller than that at other temperature zones. It is a measure of the rate of vulcanization based on the difference between optimum vulcanization time, t_{90} and incipient scorch time, t_s . Vulcanization as well as scorch was very sensitive to temperature condition. As shown in Table 3, it can be found that the effect of foaming temperature or carbon black content on the cure rate index is different. Cure rate index gradually increased with the increasing carbon black content but there was no significant rise. Meanwhile, the increase of the foaming temperature accelerated the cure rate index. It is obvious that the cure rate index is more sensitive to the vulcanizing temperature than to filler content.

2. Foaming Characteristics

To investigate the effects of foaming temperature and carbon black content on the foaming characteristics, the apparent densities and expansion ratios of the NRs foamed at five temperature zones with different filler content were measured and shown in Table 3. The density of the foamed NR increased with the increasing carbon black content, while it decreased with the increase of foaming temperature. One may explain such behavior in the following way. It is common that the density increases with the increasing filler content due to the higher density of filler. There, however, is a different phenomenon in foaming temperature. The density of gas cells inside the rubber matrix increases upon increase of foaming temperature, whereas their volume is enlarged by the thermal expansion effect. This will affect the volume fraction of carbon black as reinforcing filler for the rubber matrix; it will affect the mechanical properties as well. In other words, the dilution of carbon black will increase, so the reinforcement of the rubber matrix will be reduced and consequently

the sample will become weaker. This can be also supported by the results of expansion ratios. That can be closely related with the time difference between the decomposition temperature of blowing agent and curing temperature. It has been reported that curing temperature should not be prior to and not be too close to or far from the decomposition of blowing agent. Therefore, the control of curing temperature is very important for foaming. In this study, with the highest blowing efficiency, the lowest foam density for the foamed NRs was achieved at 165 °C.

To obtain an empirical relation describing the dependence of the volume fraction of carbon black, ϕ_c , on the foaming, one may suggest the following ideal and simple model.

Let us consider the volume fraction of carbon black in the unfoamed sample ϕ_c^0 as

$$\phi_c^0 = \frac{V_c}{V_t} = \frac{m_c}{m_t} \cdot \frac{\rho_t}{\rho_c} \quad (3)$$

where V_c , m_c , ρ_c and V_t , m_t , ρ_t are the volume, mass and density for carbon and rubber matrix, respectively. For example, by substituting the following NF-1 values, $m_c=15$ g (variables, 30 g, 50 g, 70 g), $\rho_c=1.8 \text{ g cm}^{-3}$, $m_t=140.4$ g (variables, 155.4 g, 175.4 g, 195.4 g), $\rho_t=0.93 \text{ g cm}^{-3}$, one obtains $\phi_c^0 \sim 0.06, 0.1, 0.15$ and 0.19 for NF-1, NF-2, NF-3 and NF-4, respectively.

The relation between the volume fraction of carbon black for foamed NRs ϕ_c and unfoamed NRs ϕ_c^0 , could be expressed as

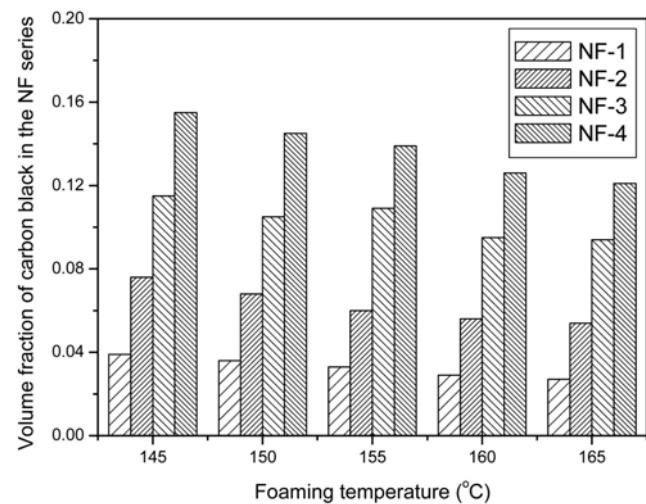


Fig. 1. Variation of the carbon black volume fraction in the foamed NRs as a function of foaming temperature and filler content.

$$\phi_c = \frac{\rho_f \phi_c^0}{\rho_f} \quad (4)$$

where ρ_f is the measured apparent density of the foamed sample. Fig. 1 presents the effect of the carbon black content and foaming temperature on the variation of volume fraction of the carbon black both in the unfoamed sample and in the foamed sample increased with the increasing filler loading, while the volume fraction value of carbon black in the foamed sample was greatly smaller than that of carbon black in the unfoamed sample due to the foaming process.

Foams are three-dimensional agglomerations of gas bubbles, separated from each other by thin sections of polymer. For a finished flexible NR foam like shown in Fig. 2, the void areas as "cells" are artifacts of gas bubbles introduced into the reacting mixture early in its existence. The thin, geometrical structures separating the void areas are made up of the polymer formed from the various reactions.

Microscopic studies were made for the NRs foamed at different foaming temperatures and carbon black contents. Micrographs of NF-1, NF-2, NF-3 and NF-4 samples at five temperatures are shown in Figs. 3, 4, 5, and 6, respectively. The thickness of each of the struts formed inside the rubber matrix decreased with the increasing foaming temperature, while it increased with the increasing carbon black content. For the shapes of the bubbles with foaming temperature and carbon black content, they are almost spherical at low temperature and at high carbon black content but show polyhedral shapes with increasing foaming temperature and decreasing carbon black content. In the early stages of foaming, when the gas volume is small,

bubbles are spherical. As the bubble volume grows, however, the fluid phase becomes insufficient to maintain the spherical shape, so that the bubbles take on polyhedral shapes, with the fluid distributed in thin membranes between two adjacent bubbles. In other words, it is difficult for spherical bubbles to maintain their shape because gas tends to diffuse from the smaller bubble into the larger one, resulting in the destruction of spherical shape. Therefore, some of the spherical bubbles changed into a distorted spherical shape or polyhedral shape. In addition, with the increase of carbon black, rubber matrix was not enough in volume fraction for foaming, resulting in the formation of thick struts. The increase of foaming temperature, however, made foaming efficiency higher, leading to the thin struts. It is clear from the micrographs that the NRs foamed at 165 °C show higher foaming efficiency, supporting the density and expansion ratio results shown in Table 4.

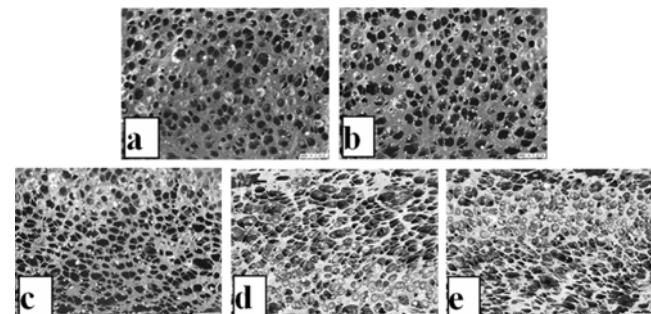


Fig. 4. Microscopy photographs of the NF-2 series as a function of foaming temperature and filler content.

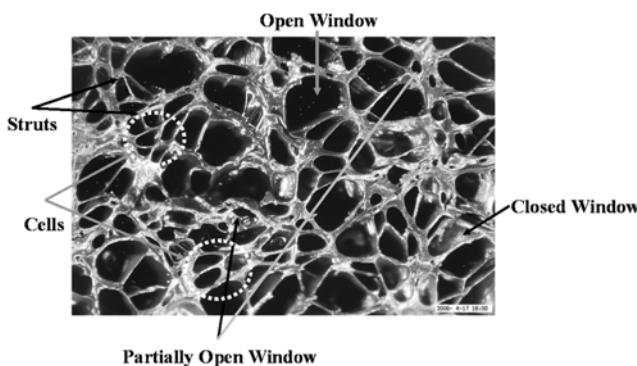


Fig. 2. Flexible natural rubber foam at 100× magnification.

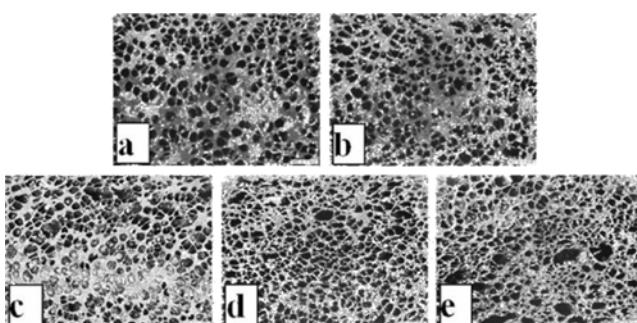


Fig. 3. Microscopy photographs of the NF-1 series as a function of foaming temperature and filler content.

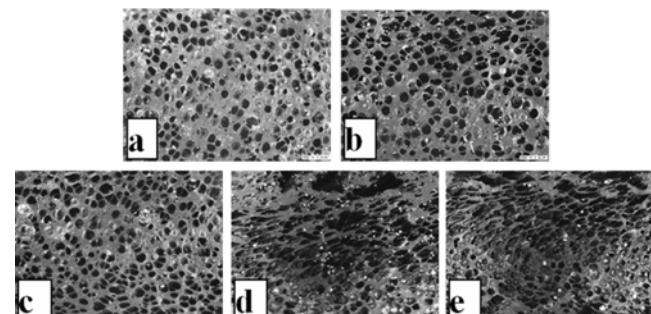


Fig. 5. Microscopy photographs of the NF-3 series as a function of foaming temperature and filler content.

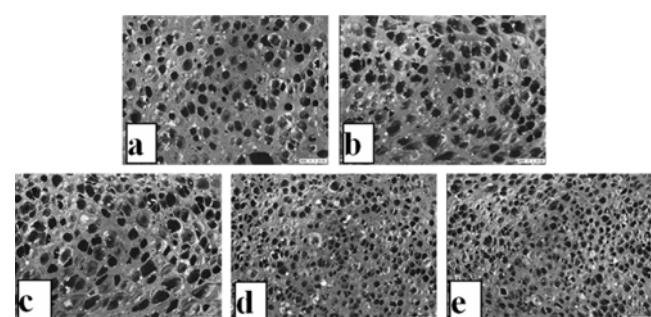
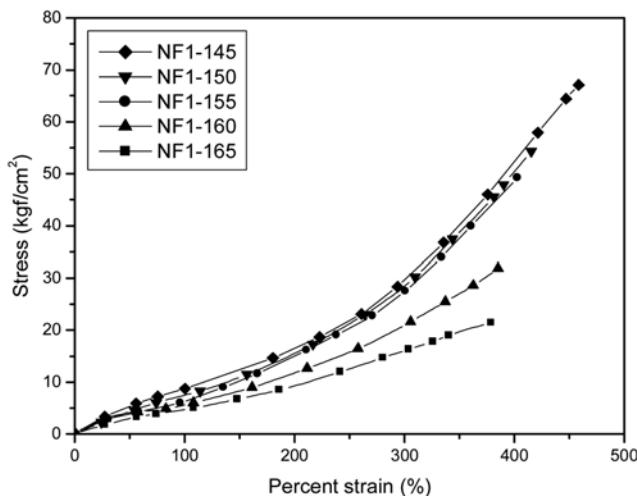
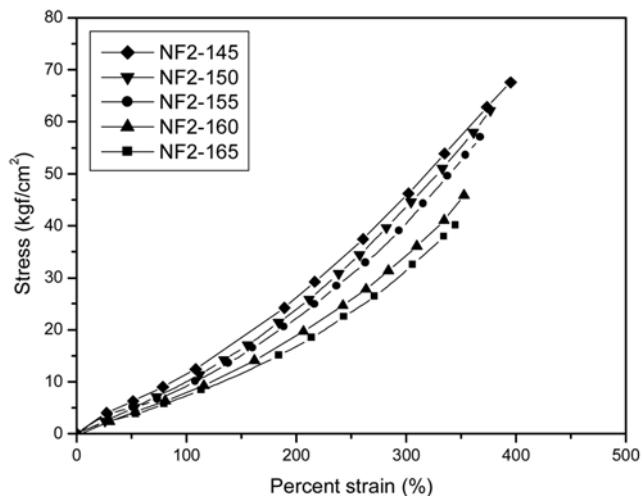


Fig. 6. Microscopy photographs of the NF-4 series as a function of foaming temperature and filler content.

Table 4. Variation of tensile properties and hardness of the NR foams

Temp. (°C)	Tensile strength (kgf/cm ²)				Elongation at break (%)				Tear strength (kgf/cm ²)				Hardness (shore C)			
	NF1	NF2	NF3	NF4	NF1	NF2	NF3	NF4	NF1	NF2	NF3	NF4	NF1	NF2	NF3	NF4
145	67.1	67.6	72.8	77.9	458	395	208	244	16.5	16.9	20.6	17.6	44	57	59	65
150	64.8	62.3	64.5	64.8	415	376	292	237	13.8	15.8	16.9	16.9	42	45	50	64
155	59.8	59.7	61.3	60.2	402	367	290	224	13.3	13.7	16.3	14.0	35	40	49	57
160	31.8	45.9	45.8	53.7	391	357	281	195	12.0	11.8	15.0	13.2	34	39	43	53
165	20.9	42.2	39.3	47.3	375	346	273	183	11.0	10.8	13.0	12.0	33	38	41	52

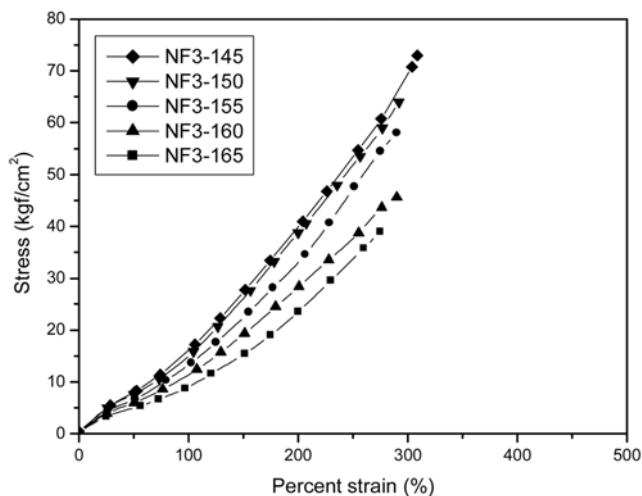
**Fig. 7. Stress-strain curves of the NF-1 series as a function of foaming temperature.****Fig. 8. Stress-strain curves of the NF-2 series as a function of foaming temperature.**

3. Mechanical Properties

The effects of foaming temperature and carbon black content on the tensile properties and hardness of the foamed NRs are shown in Table 4. It was found that the tensile strength increased steadily with an increase of carbon black content, but there was little effect as the foaming temperature increased. The tensile strength of the compounds increased with the increasing carbon black content due to the reinforcing effect of carbon black. The tensile strengths of NRs foamed at 165 °C were lower than those at other temperature zones due to lower density, indicating better blowing efficiency; the NRs foamed at 165 °C indicating the lowest blowing efficiency and highest density showed better tensile properties.

The elongation at the break dropped continuously with the increasing foaming temperature and carbon content. This trend may be attributed to the rigid carbon black-rubber interface upon increasing content of carbon black. This is a similar case as increasing particulate filler in the rubber compounds. It was found that the increment in filler content resulted in a reduction of the deformability of a rigid interface between the filler and the rubber matrix. Furthermore, in this study for elongation at break, foams with high blowing efficiency were seen to be inferior to those with low blowing efficiency.

Tear strength is the force per unit thickness used to initiate a rupture or tear of the materials. Tear strengths of the samples increase continuously with carbon black content due to the reinforcing effect of carbon black, which is similar to the results of tensile strength.

**Fig. 9. Stress-strain curves of the NF-3 series as a function of foaming temperature.**

However, tear strengths decreased with the increasing foaming temperature.

The hardness of the NR foams increased with the increasing carbon black content, while decreased with the increasing foaming temperature as shown in Table 4. This can be attributed to the carbon black amount for the former and the more foaming efficiency for the latter.

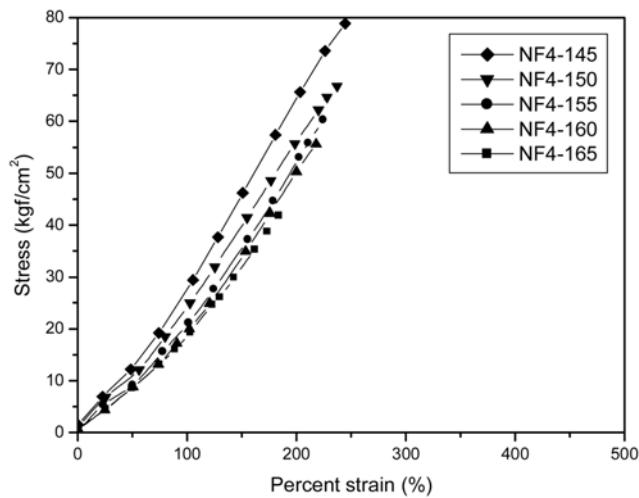


Fig. 10. Stress-strain curves of the NF-4 series as a function of foaming temperature.

The nature of the deformation of the NR foams under an applied load can be understood from the stress-strain curves. The stress-strain curves as a function of foaming temperature and carbon black content are given in Figs. 7, 8, 9 and 10. It can be seen that NR foams can accommodate more stress, while exhibiting lower elongation with the increasing carbon black content. Meanwhile, as the foaming temperature increased, stress decreased together with elongation at break due to the thinner thickness of each of the struts formed inside the rubber matrix.

CONCLUSION

With increasing filler content and foaming temperatures, the cure rate indices of the NRs foams rose and the difference between the curing time and scorch time decreased. The optimal temperature of the vulcanization and foaming of NRs in this study only for blowing efficiency was 165 °C. The densities of NRs foamed at 165 °C

were lower than those at other temperature zones, supporting the foaming efficiency results. The tensile strength of the compounds increased with the increasing filler content because of the reinforcing effect of carbon black. For the foaming temperature, the tensile strength decreased in the following order, 145 °C, 150 °C, 155 °C, 160 °C and 165 °C, which was closely related with density and expansion ratio results. The elongation at break dropped continuously with increasing foaming temperature and carbon black content. Like the tensile strength, tear strength and modulus of the samples increased continuously with carbon black content, while decreased with the increasing foaming temperature. As a result, it is found that foaming temperature is a clear main factor for curing characteristics, while mechanical properties are more closely related with filler content than with foaming temperature.

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