

Effects of Foaming Temperature and Carbon black Content on the Cure Behaviors and Foaming Characteristics of the Natural Rubber Foams

Joon-Hyung Kim, Kyo-Chang Choi[†], Jin-Min Yoon, and Soo-Yeon Kim
R&D Center, Hwa-Seung Rubber & Automotives, 147-1,
Gyo-Dong, Yangsan Gyeongnam 626-210, South Korea
(Received June 13, 2006, Revised & Accepted August 23, 2006)

발포온도와 카본블랙 함량이 천연고무 발포체의 가황거동 및 발포특성에 미치는 영향

김 준 형 · 최 교 창[†] · 윤 진 민 · 김 수 연
화승알앤에이
(2006년 6월 13일 접수, 2006년 8월 23일 수정 및 채택)

ABSTRACT : To investigate the influence of the foaming temperature and carbon black content on the cure behaviors and foaming characteristics of the foams, natural rubber (NR) was foamed at five temperature zones (145, 150, 155, 160 and 165 °C) and different feeding ratios of the carbon black. A decreasing trend of the scorch time, t_{s2} and cure time, t_{90} was observed upon increasing foaming temperature and carbon black content. The optimal temperature for vulcanization and foaming of NRs in this study was considered to be 165 °C where density of the foamed NRs is lower than those at other four temperature regions. The cure rate index of the NRs foamed at 145 °C is smaller than those at 150, 155, 160 and 165 °C. The results of the expansion ratio and micrographs of the foamed NRs were founded to support the density characteristics. The thickness of each of the struts formed inside the rubber matrix decreases with increasing the foaming temperature, while it increases with increasing the carbon black content.

요 약 : 본 연구에서는 발포체의 가황거동과 발포특성에 발포온도 및 카본블랙 함량이 미치는 영향을 조사하기 위해 카본블랙을 변량 배합하고 145 °C에서 165 °C까지 5 °C 간격으로 발포하여 천연고무 발포체를 제조하였다. 발포온도 및 카본블랙 함량이 증가함에 따라 t_{s2} 그리고 t_{90} 의 감소 경향이 관찰되었다. 본 연구에서 천연고무의 발포 가황특성의 최적 온도는 165 °C였으며 이때 발포된 천연고무 밀도가 가장 낮은 것으로 확인되었다. 145 °C에서 발포된 천연고무 발포체의 가속도지수가 가장 작은 값을 보였다. 발포 천연고무의 발포 및 모폴로지 특성으로부터 발포체의 밀도 특성을 확인할 수 있었다. 고무내부에 생성된 각 발포 격벽의 두께는 발포온도가 증가함에 따라 감소하는 반면 카본블랙 함량 증가와 더불어 증가함을 보였다.

Keywords : vulcanization temperature, cure behavior, foaming, cure rate index

[†]대표저자(e-mail : lionseven@hsrna.com)

I. Introduction

Typical applications for sponge rubbers include automotive weather-stripping, gaskets, pipe insulation etc. The manufacturing methods include either low- or high pressure moulding and extrusion. Gas producing chemicals (blowing agents) are incorporated into the sponge rubber compounds. During the curing cycle these chemicals release gas that gives rise to the cellular structure of the sponge product. Examples of important commercial blowing agents are hydrazides, dinitrosopentamethylene tetramine, and azodicarboamide. Without activation, they generate nitrogen gas at temperatures of 104, 192, and 202 °C, respectively. Furthermore, activators and other chemicals of the rubber compound lower the decomposition temperature and the two processes, blowing (expansion) and vulcanization, run simultaneously during the curing cycle.^{1,2} 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. Since the 1940s cellular polymers have been commercially accepted in a wide variety of applications because of advantages of light weight, buoyancy, cushioning performance, thermal and acoustic insulation, impact damping, and cost reduction.³ 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 the broad range of cellular synthetic polymers in use today.

Most uses of rubber foams have been derived from the desired combination of low density and some other physical properties. Although a foamed rubber is widely manufactured and is in service all over the world, the available articles concerning their electrical, mechanical and physicomachanical 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.^{4,5}

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.⁶

To obtain optimal foam expansion and good physical properties of the foams, optimal cross-linking is the most critical requirement. In this study, the NR foams were prepared at various temperatures (145, 150, 155, 160 and 165 °C) and different feeding contents of the filler (15, 30, 50 and 70 phr). The influence of the foaming temperature and reinforcing filler content on the cure behaviors and volume fraction of the carbon black of the foams were studied. The density and expansion ratio of the foamed NRs were also studied and a microscope is used to investigate the effects of the foaming temperature and filler content on the morphologies of the foamed NRs.

II. Experimental

1. Materials and sponge rubber preparation

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 mercaptobenzothiazyl disulfide (MBTS) were of commercial grade. As a blowing agent and blowing activator respectively, *N,N*-dinitrosopentamethylene tetramine (DPT) and Cellex-A[®] were received from Kumyang, Korea.

Table 1. Formulations of the NR compounds.

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

^a Parts per hundred rubber

^b NF-1, 2, 3, and 4; N refers to NR, F foam and 1-4 filler contents (15, 30, 50, and 70, respectively).

NR compounds were prepared in four different combinations. NR was compounded using a two-roll mill according to the recipe shown 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 different temperatures. The compounded NRs were then compression molded along the mill grain direction using an electrically heated hydraulic press at different temperatures under a pressure of 14 kgf/cm² for their optimum cure time, t_{90} . Efficient blowing agent (DPT) and blowing promoter (Cellex-A[®]) were carefully selected by TGA analysis.

2. Curing and foaming characteristics

Cure characteristics were studied at five temperature zones using 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, MIRAGE). 2 × 2 cm sample was cut out of a foam, and its thickness, t_1 (cm) and weight, W_2 (g) were measured and expansion ratio was calculated from the following equation.⁷

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

where t_1 is the thickness and W_2 is the weight of the sample.

The morphology of the NR foams was analyzed using an microscope (Hi Scope Advanced KH-3000). A thin slice cut of the foamed NR was magnified with a microscope.

III. Results and discussion

The results obtained in this study are discussed with respect to the cure properties, foaming characteristics and mechanical properties of the natural rubbers foamed in the five temperature regions from 145 °C to 165 °C by 5 °C interval.

1. Blowing promoter and Cure characteristics

To investigate the effect of a blowing promoter on the decomposition temperature of a blowing agent, a mixture of DPT and Cellex-A[®] and their TGA thermograms were obtained. As shown in Figure 1, the decomposition temperature of a mixture of DPT and Cellex-A[®] moved lower than that of single DPT. DPT-A refers to a mixture of DPT and Cellex-A[®]. Decomposition temperature changed from 206 °C to 138 °C by the addition of a blowing promoter, Cellex-A[®].

The cure characteristics of the NRs foamed at different temperatures with different carbon black contents were presented at Figure 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

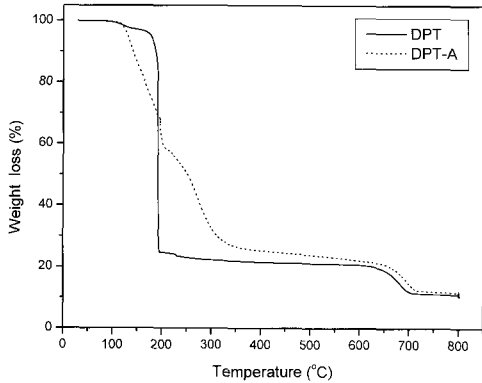


Figure 1. Effect of the blowing promoter on the decomposition of the blowing agent.

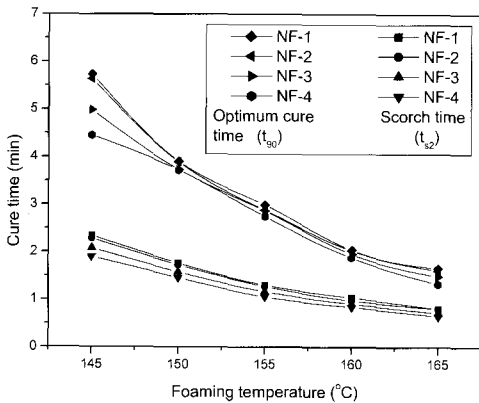


Figure 2. Variation of the t_{s2} and t_{90} of the foamed NR as a function of the foaming temperature and filler content.

scorch time decreases with increasing foaming temperature and filler loading. This observation may be attributed to the viscosity increase with increasing the carbon black content and pre-vulcanization along with the rising foaming temperature. Therefore, the shorter time is required for beginning of the vulcanization process for the NR foam compounds. A decreasing trend of the optimum cure time, t_{90} was also observed upon increasing foaming temperature and carbon black content. Figure 3 shows the variation of minimum torque and maximum torque with increasing the foaming temperature and carbon black content. A minimum torque, ML is a measure of stiffness of the unvulcanized test

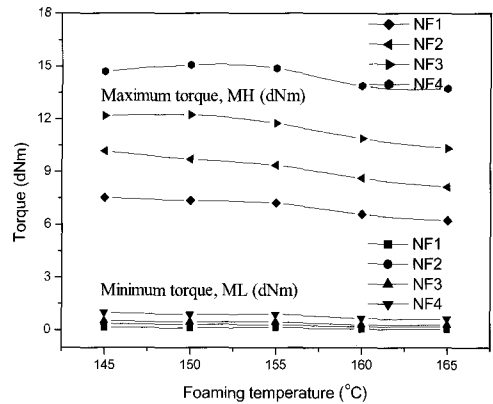


Figure 3. Variation of the ML and MH of the foamed NR as a function of the foaming temperature and filler content.

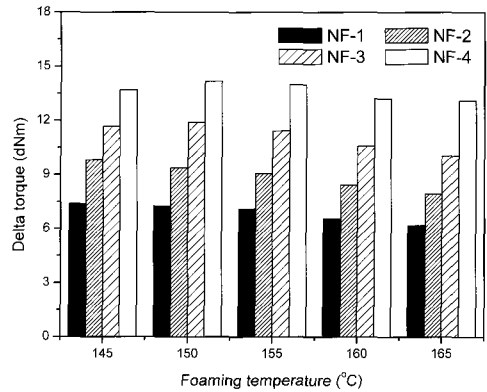


Figure 4. Variation of the delta torque of the foamed NR as a function of the foaming temperature and filler content.

specimen taken at the lowest point of the cure curve. It can be seen that the minimum torque increases with increasing the carbon black content but decreases slightly with increasing the foaming temperature. The former is due to the viscosity increase and decrease of the relative amount of process oil with the increasing carbon black content; the latter is due to the viscosity decrease by the plastic deformation with increasing the 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

(Figure 4) between the maximum and minimum torques 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 the foaming temperature due to the decrease of the force applied to the rotating disk when the blowing efficiency of NR foam increases.

Figure 5 shows the cure rate index of the foamed NRs with various foaming temperatures and carbon black contents. The cure rate index is calculated as follows:⁸

$$\text{Cure rate index} = \frac{100}{t_{90} - t_{s2}}$$

Cure rate index at 145 °C is smaller than those at the other temperature zones. Cure rate index is a measure for rate of vulcanization based on the difference between the optimum vulcanization time, t_{90} and incipient scorch time, t_{s2} . Vulcanization as well as scorch is very sensitive to temperature condition. As shown in Figure 5, 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 increases with increasing the carbon black content but there is no significant rise. Meanwhile, the increase of the foaming temperature accelerates the cure rate index. It is obvious that the cure rate index is more sensitive to the vulcanizing temperature than to the 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 the five temperature zones with different filler contents were measured and depicted in Figures 6 and 7, respectively. The density of the foamed NR increases with the increasing carbon black content, while it decreases with the increase of foaming temperature. One may explain such

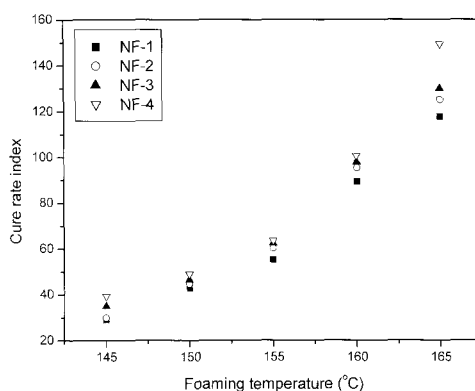


Figure 5. Variation of the cure rate index of the foamed NR as a function of the foaming temperature and filler content.

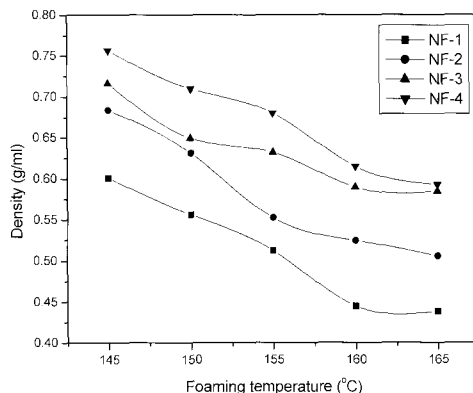


Figure 6. Variation of the density of the foamed NR as a function of the foaming temperature and filler content.

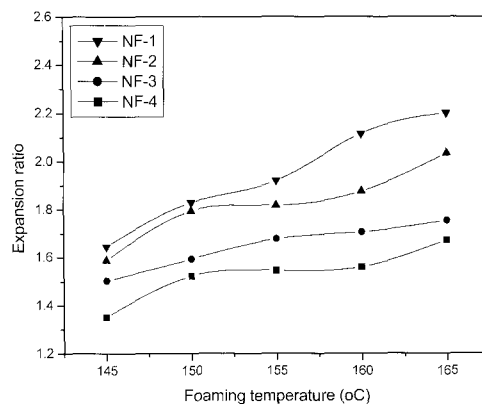


Figure 7. Variation of the expansion ratio of the foamed NR as a function of the foaming temperature and filler content.

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 with increase of the 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. This will also 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 NR is 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

$$\phi_c^0 = \frac{V_c}{V'} = \frac{m_c}{\rho_c} \cdot \frac{\rho_t}{m_t} \quad (1)$$

where the V_c , m_c , ρ_c and V_b , m_b , 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), $\rho_c = 1.8$ gcm⁻³, $m_t = 140.4$ g (variables, 155.4 g, 175.4 g, 195.4 g), $\rho_t = 0.93$ gcm⁻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 fractions of carbon black for foamed NRs ϕ_c and unfoamed NRs ϕ_c^0 could be expressed as

$$\phi_c = \frac{\rho_f}{\rho_t} \phi_c^0 \quad (2)$$

where the ρ_f is the measured apparent density of the foamed sample. Figure 8 presents the effect of the carbon black content and foaming temperature on the variation of volume fraction of the carbon black in foamed NR. In that, the volume fraction of carbon black both in the unfoamed sample and in the foamed sample increases with the increasing filler loading, while the volume fraction value of carbon black in the foamed sample is greatly smaller than that of carbon black in the unfoamed sample due to the foaming process.

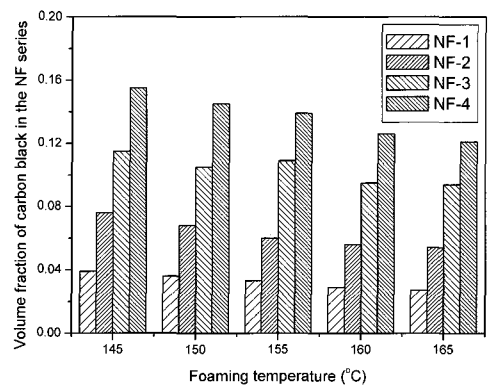


Figure 8. Variation of the carbon black volume fraction in the foamed NRs as a function of the foaming temperature and filler content.

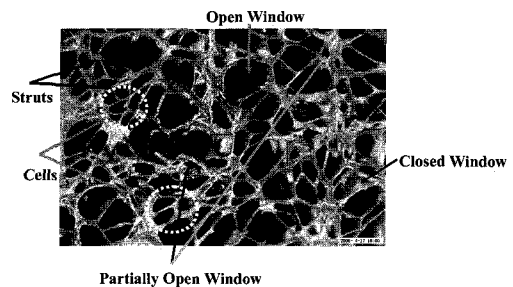


Figure 9. Image of the flexible natural rubber foam at 100 magnification.

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 Figure 9, the void areas as "cells" are artifacts of gas bubbles that were 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 the different foaming temperatures and carbon black contents. Micrographs of NF-1, NF-2,

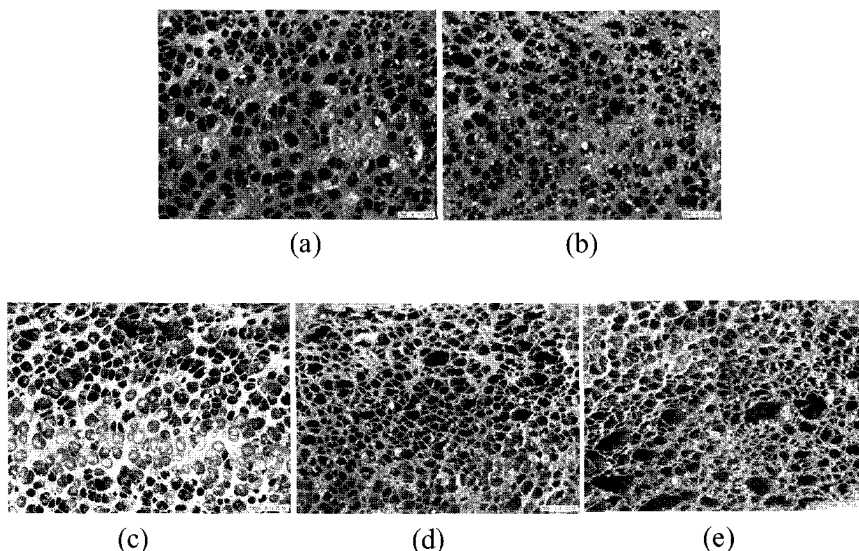


Figure 10. Microscopic photographs of the NF-1 foams prepared at 145 (a), 150 (b), 155 (c), 160 (d), and 165°C (e).

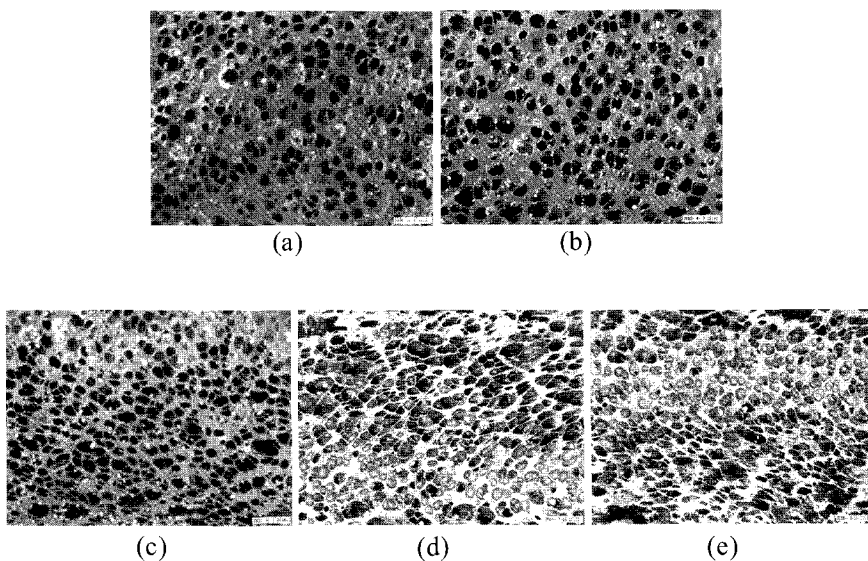


Figure 11. Microscopic photographs of the NF-2 foams prepared at 145 (a), 150 (b), 155 (c), 160 (d), and 165°C (e).

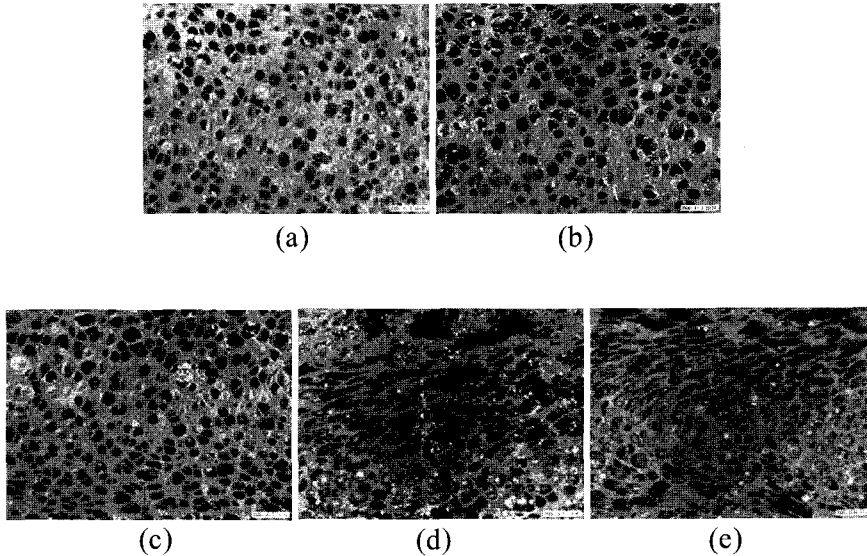


Figure 12. Microscopic photographs of the NF-3 foams prepared at 145 (a), 150 (b), 155 (c), 160 (d), and 165°C (e).

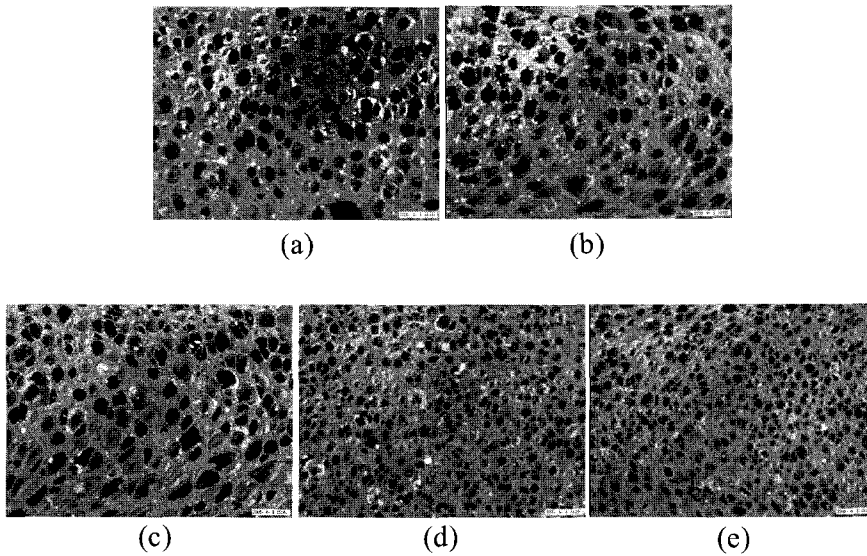


Figure 13. Microscopic photographs of the NF-4 foams prepared at 145 (a), 150 (b), 155 (c), 160 (d), and 165°C (e).

NF-3 and NF-4 samples at the five temperatures are shown in Figures 10, 11, 12 and 13, respectively. The thickness of each of the struts formed inside the rubber matrix decreases with the increasing foaming temperature, while it increases with the increasing carbon black content. For the shapes of the bubbles with the 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 the foaming temperature and decreasing the carbon black content. In the early stages of foaming, when the gas volume is small, bubbles are spherical in shape. As the bubble volume grows, however, the fluid phase

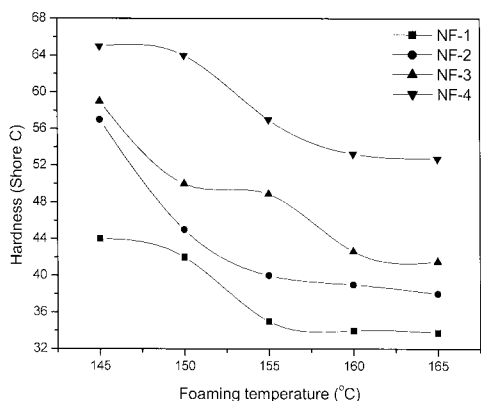


Figure 14. Variation of the hardness of the foamed NR as a function of the foaming temperature and filler content.

becomes insufficient to maintain the spherical shape, so that the bubbles take on polyhedral shapes, with the fluid distributes in thin membranes between two adjacent bubbles. In other words, it is difficult for bubbles in spherical shape to maintain their shape because gas tends to diffuse from the smaller bubble into the larger one, resulting into the destruction of spherical shape.⁹ Therefore, some of the bubbles in spherical shape changed into the distorted spherical shape or polyhedral shape. In addition, with the increase of carbon black, rubber matrix is not enough in volume fraction for foaming, resulting into the formation of thick struts. The increase of foaming temperature, however, makes 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 Figure 6.

The hardness of the NR foam increases with the increasing carbon black content, while decreases with the increasing foaming temperature as shown in Figure 14. This can be attributed to the carbon black amount for the former and the more foaming efficiency for the latter.

IV. Conclusion

With increasing the filler content and foaming

temperatures, the cure rate indices of the NRs foams rise and the difference between the curing time and scorch time decreases. The optimal temperature of the vulcanization and foaming of NRs in this study only for blowing efficiency is 165 °C. The densities of NRs foamed at 165 °C are lower than those at other temperature zones, supporting the foaming efficiency results. The thickness of each of the struts formed inside the rubber matrix decreases with the increasing foaming temperature, while it increases with the increasing carbon black content. The hardness of the NR foams increases with the increasing carbon black content, while decreases 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.

References

1. D. Datta, J. Kirchhoff, D. Mewes, W. Herrmann and G. Galinsky, "An ultrasonic technique to monitor the blowing process in sponge rubbers", *Polym. Test.*, **21**, 209 (2002).
2. N. M. Bikales, "Encyclopedia of Polymer Science and Technology", John Wiley & Sons, New York (1965).
3. M. S. Kim, C. C. Park, S. R. Chowdhury and G. H. Kim, "Physical Properties of Ethylene Vinyl Acetate Copolymer/Natural Rubber Blend Based Foam", *J. Appl. Polym. Sci.*, **94**, 2212 (2004).
4. R. Joseph, "Handbook of Polymer Foams", Rapra Technology, UK (2004).
5. W. Hofmann, "Rubber Technology Handbook", Oxford University Press, New York (1989).
6. A. El. Lawindy, K. A. El-Kade, W. Mahmoud and H. Hassan, "Physical studies of foamed reinforced rubber composites Part I. Mechanical properties of foamed ethylene-propylene-diene terpolymer and nitrile-butadiene rubber composites", *Polym. Int.*, **51**, 601 (2002).
7. N. Uejykkoku and Y. Nakatsu, "Polyolefin based crosslinked foam", U.S. Patent 5,786,406 (1996).
8. C. Nakason, A. Kaesamna, and K. Eardorod, "Cure

and mechanical properties of natural rubber-g-poly (methyl methacrylate)-cassava starch compounds", *Mater. Lett.*, **59**, 4020 (2005).

9. F. A. Shutov, "Polymeric Foams and Foam Technology", Hanser, Cincinnati (2004).