

# Mechanical and Morphological Properties of Cellular NR/SBR Vulcanizates Under Thermal and Weathering Ageing

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**ABSTRACT:** The effects of addition of two chemical blowing agents in cellular rubber blend of natural rubber (NR) and styrene-butadiene rubber (SBR) at a fixed blend ratio of 1 : 1 on cure characteristics, and mechanical and morphological properties were investigated. The chemical blowing agents used in this work were Oxybis (benzene sulfonyl) hydrazide (OBSH) and Azo dicarbonamide (ADC). Three different fillers, fly ash (FA) particles, precipitated silica, carbon black (CB) at their optimum concentrations of 40 phr were used, the FA and silica particles being chemically treated by bis-(3-triethoxysilylpropyl) tetrasulphide. The results suggested that the overall cure time decreased with OBSH and ADC contents. The OBSH was more effective in cure-acceleration of the NR/SBR blend than the ADC. The NR/SBR vulcanized foams produced by OBSH and ADC agents had closed-cell structures. The specific density and mechanical properties of

the blend tended to decrease with increasing blowing agent content. The CB gave NR/SBR foams with smaller cell size, better cell dispersion, and higher mechanical properties than the precipitated silica and FA particles. The heat ageing and weathering resulted in an increase in tensile modulus and hardness, but lowered the tensile strength, ultimate elongation and tear strength. The elastic recovery for cellular NR/SBR vulcanizates with FA was superior to that with CB and silica, the elastic recovery of the blends decreasing with blowing agent content. Resilience property was improved by the presence of gas phases. The optimum concentration of OBSH and ADC to be used for NR/SBR vulcanizates was 4 phr. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2816–2827, 2009

**Key words:** cellular rubber; blowing agent; natural rubber; mechanical properties; foam

## INTRODUCTION

Cellular rubbers or expanded rubbers are composite materials made up of a rubber matrix and a gas phase. Such materials have been used commercially in a wide range of applications including thermal insulations, gaskets, buoyancy, and impact sound deadening products. The mechanical properties of cellular rubbers are related to both the foam cells and the properties of the rubbers used. Structural variables include rubber crosslink density, foam cell density, cell structure, average cell size, and the cell geometry (open or closed cell). The processing of rubber foams involves curing a vulcanized rubber compound that contains a blowing agent in a mould under high temperature and pressure until the blowing agent has decomposed on opening the mould, allowing expansion of the rubber compound.<sup>1</sup>

The morphological and mechanical properties of cellular rubbers are known to be affected by the type and content of blowing agents used.<sup>2–6</sup> Sombatsompop and Lertkamolsin<sup>2</sup> investigated the effects of additions of Oxybis (benzene sulfonyl) hydrazide (OBSH) and Azo dicarbonamide (ADC) blowing agents on density, degree of crosslinking, and swelling behaviour in cellular natural rubber (NR) vulcanizates. They showed that apparent foam density and crosslink density for NR vulcanizates decreased with increasing blowing agent content. The rubber swelling greatly changed with OBSH, but unaffected by ADC content. Similar behavior was also observed for synthetic rubbers.<sup>3,4</sup> The mechanical properties of cellular ethylene-propylene rubber (EPDM) usually decreased with increasing blowing agent content and this could be explained by a decrease in crosslink density during foam expansion.<sup>3</sup> In rubber composites, the mechanical properties of the foam vulcanizates are dependent on the type, concentration, filler, fiber orientation, and adhesion between the fiber (or filler) and the rubber matrix.<sup>5,6</sup> Lin et al.<sup>5</sup> studied microstructure and mechanical properties of nylon 6,6-fiber/NR foam composites with and without surface treatment of the fiber. The results suggested that the addition of nylon-fibers improved the overall

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mechanical properties of the rubber foams. The mechanical properties of the rubber composite foams were strongly dependent on the density of the microcellular foam, fiber orientation. The relationship between the foam density and mechanical properties was also studied by Kim et al.,<sup>6</sup> who examined the influences of foaming temperature and carbon black (CB) content on cure behavior and mechanical properties for the NR foams. They found that the densities and tensile strength of the NR foam decreased with increasing curing temperature. Increasing CB content increased the tensile modulus, tensile strength and tear strength, but decreased the elongation at break. Recent literatures show that published articles on the structure-property relationships of expanded single-rubbers are extensively evidenced, but there has been very little attention given to expanded rubber blend and rubber composite systems.

Fly ash (FA) particles obtained from thermal power plant stations has been reported as a natural silica that gave good dynamic properties and compression set when used with appropriate silane coupling agents.<sup>7,8</sup> According to a previous work,<sup>8</sup> FA particles contained silica approximately 40–46 wt % with similar silanol groups on its surfaces. Comparing with precipitated silica, FA particles yield superior elasticity. As a result, FA could become alternative reinforcing filler for cellular rubbers, both natural and synthetic rubbers,<sup>9,10</sup> and rubber blends<sup>11,12</sup> vulcanizates for gasket and cushion applications.

This article was aimed to extend our works<sup>7–12</sup> on use of silica-based FA particles in rubber materials. This present work reported cure characteristics, and (mechanical and morphological properties of cellular rubber vulcanizates of natural rubber (NR)) and styrene-butadiene rubber (SBR) blend varying types and contents of chemical blowing agents (OBSH and ADC) and fillers (CB, precipitated silica, silica-based FA particles). The changes in mechanical properties of the foamed NR/SBR vulcanizates were also monitored before and after thermal and weathering ageing. It should be noted that the filler type, ageing conditions, and the mechanical properties tested, which were performed in this work, were designed and selected based on potential applications in thermal insulation, cushions, gaskets, buoyancy and impact sound deadening products.

## EXPERIMENTAL

### Raw materials

#### Rubber

NR (NR, STR20) used was supplied by Huay Chuan Co., Ltd., (Bangkok, Thailand). SBR (SBR1712) was supplied by BST Elastomers (Bangkok, Thailand) with a styrene content of 24.5%, 28.8% oil, and 5.7% organic acid.

#### Fillers

CB (HAF-N330 by Thai Carbon Black Public Co., Ltd., Bangkok, Thailand). The CB had an average particle size of 32  $\mu\text{m}$ . Commercial precipitated silica (Tokusil 233) was designated as P<sub>Si</sub> and supplied by Tokuyama Siam Silica (Bangkok, Thailand) having an average particle size of 50  $\mu\text{m}$ , pH of 6.8, a bulk density of 0.232  $\text{g}/\text{cm}^3$ , and a BET surface area of 128  $\text{m}^2/\text{g}$ . Silica from FA particles (FASi) was also used as alternative filler in this work. The FA particles were supplied by Mae Moh Power Station of KNR Group Co., Ltd. (Lampang, Thailand) having an average particle size of 125  $\mu\text{m}$ . The characteristics (dimensions, average particle size, shape, and surface area, density, and pH) of the FA particles can be found in elsewhere.<sup>7,11</sup> According to our previous results<sup>7,8,11</sup> on chemical compositions of the FA particles, the major component of FA was  $\text{SiO}_2$  (46.0%). The FA used had the same functional groups (e.g., silanol and siloxane groups at wavenumbers of around 3400 and 1100  $\text{cm}^{-1}$ , respectively) as the commercial silica. The required silica (FASi) content in the FA particles added to the NR/SBR compound was calculated based on the fact that there was 46.0 wt % silica in FA.

#### Silica-surface treatment

Bis-(3-triethoxysilylpropyl) tetrasulphide (trade name designated as Couplink 89C),  $[(\text{C}_2\text{H}_5\text{O})_3\text{Si}-(\text{CH}_2)_3\text{S}_4-(\text{CH}_2)_3\text{Si}-(\text{C}_2\text{H}_5\text{O})_3]$ , was used as a chemical coupling agent for surface treatment of precipitated silica and FA particles. The Couplink 89C was supplied by Behn Meyer Chemical Co. (Bangkok, Thailand). The experimental procedure for surface treatment by Couplink 89C was the same as used for bis-(3-triethoxysilylpropyl) tetrasulfane (Si69) which can be found in previous studies.<sup>8,11</sup> In this work, the Couplink 89C content used was 2.0 %wt of silica.

#### Chemical blowing agents

Oxybis (benzene sulfony) hydrazide (OBSH) and modified ADC (Grade Supercell-522), supplied by A.F. Goodrich Chemical Co., Ltd., (Bangkok, Thailand) were used as the chemical blowing agents. According to the suppliers, both blowing agents had the decomposition temperature of around 160°C.

### Rubber blending and sample preparation

#### Compounding and vulcanization of cellular NR/SBR rubber

In this work, the formulations of NR/SBR blend compounds reinforced with CB, precipitated silica and silica-based FA particles in parts per hundred rubber

**TABLE I**  
**Vulcanizing Recipes for NR/SBR Vulcanizates**

Ingredients	Function	Content (phr)
1. NR : SBR (1 : 1)	Matrix	100
2. Zinc oxide	Activator	5.3
3. Stearic acid	Activator	3.0
4. Mercaptobenzoazole (MBT)	Accelerator	1.0
5. BHT	Antioxidant	1.0
6. Polyethylene glycol	Activator	5 wt % of silica
7. Filler (silica from FA, silica or CB)	Reinforcing filler	40
8. OBSH or ADC	Blowing agent	Varied; 0, 2, 4, 6, 8, and 10
9. Sulfur	Cross-linker	1.5

(phr), are given in Table I. The blend ratio of NR : SBR used was fixed at 1 : 1.<sup>11</sup> The compounding process was commenced by masticating the NR/SBR on a laboratory two-roll mill (Yong Fong Machinery Co., Ltd., Samutsakon, Thailand) for 5 min, followed by adding the required vulcanizing agents and blowing agents on the two-roll mill for a further 35 min, the compound being then kept at 25°C with 50% relative humidity prior to further use. The resultant rubber compounds were then compression-molded to a 90% cure with a hydraulic press (LAB TECH Co., Ltd., Bangkok, Thailand) at 170 kg/cm<sup>2</sup>, using a 160°C cure temperature to produce vulcanized NR/SBR blend. It should be noted that the sample configurations (shape and size) were dependent on the type of testing standard used. The cure time used for any individual compound was pre-determined by an Oscillating Disk Rheometer (Model ODR GT 7070-S2, GOTECH Testing Machine, Taiwan) followed ASTM D2084-01 (2001) at a test temperature of 160°C before the vulcanization process proceeded.

### Characterizations

#### Cure characteristics

Cure time values of the NR/SBR compounds were measured using an Oscillating Disk Rheometer (Model ODR GT 7070-S2, GOTECH Testing Machine, Taiwan) at a test temperature of 160°C.

#### Specific density

Specific density of the cellular NR/SBR vulcanizate was determined according to ASTM D792-68 (1968) using Archimedes water replacement technique.

#### Mechanical properties

Tensile properties of NR/SBR vulcanizates were monitored in terms of modulus at 200% elongation,

tensile strength, and elongation at break using ASTM D412-03 (2003) with dumbbell-shaped samples, the tests being carried out using the universal testing machine Model Autograph AG-I, Shimadzu (Tokyo, Japan). Tear strength was determined according to ASTM D624-00 (2000) using angle-specimens (die C) and a Shimadzu tear strength testing machine. Both tensile and tear properties used a testing speed of 500 mm/min. A hardness durometer (Shore A) Model 475, PTC instruments, (MA) was used for hardness tests in accordance with ASTM D 2240-03 (2003).

#### Compression set

The test conditions and procedure of compression set testing followed ASTM D395 Method B (under a constant deflection in air). The NR/SBR sample was in a cylindrical disk form, having a diameter of 29 mm and a thickness of 12.5 mm. A space bar of 9.5 mm thick was used to maintain the compression deflection. The original thickness ( $t_o$ ) of test samples was measured by micrometer. The testing time was conditioned in an oven at 100°C for 22 h before cooled down at room temperature for 30 min and then the final thickness ( $t_i$ ) of the sample was measured. The percentage compression set can be expressed using eq. (1).

$$\% \text{Compression set} = \frac{t_o - t_i}{t_o - t_n} \times 100 \quad (1)$$

where  $t_o$  is the original thickness of the test specimen (mm);  $t_i$  is the final thickness of the test specimen (mm);  $t_n$  is distance of space bars (mm).

#### Resilience property

The resilience test was conducted using ASTM D2632-01 (2001), performed on a Wallance Dunlop Tripsometer (H.W. Wallance & Co., Ltd., Kingston, UK).

#### Heat ageing properties

The effect of heating ageing on the mechanical properties of the NR/SBR filled with CB, FASi, or PSi filler was studied through ASTM D573-04 (2004) at an oven temperature of 70°C for 96 h. The changes in mechanical properties before and after the heat ageing conditions were then evaluated.

#### Accelerated weathering test

UV and water condensation for the NR/SBR filled with CB, PSi, or FASi fillers were studied using ASTM G154-06 (2006) using a Q-UV apparatus with

**TABLE II**  
**Cure Time, Mooney Viscosity and Mechanical Properties of Solid NR/SBR Vulcanizates for Different Concentrations of CB**

Properties	CB content (phr)					
	0	20	40	60	80	100
Cure time (min : sec)	9 : 3	12 : 0	11 : 2	10 : 1	9 : 3	9 : 5
Mooney viscosity, ML (1 + 4)100°C	19	19	27	40	63	84
Property, original						
Tensile Modulus at 200% ( $\times 10^5$ Pa)	8 $\pm$ 0	17 $\pm$ 0	19 $\pm$ 1	18 $\pm$ 1	17 $\pm$ 1	13 $\pm$ 0
Tensile strength (MPa)	8 $\pm$ 0	17 $\pm$ 2	19 $\pm$ 1	18 $\pm$ 1	17 $\pm$ 1	13 $\pm$ 0
Elongation at break (%)	1099 $\pm$ 23	984 $\pm$ 19	769 $\pm$ 12	550 $\pm$ 14	362 $\pm$ 13	220 $\pm$ 9
Tear strength (kN/m)	15 $\pm$ 1	28 $\pm$ 0	48 $\pm$ 0	90 $\pm$ 0	35 $\pm$ 0	31 $\pm$ 0
Hardness (Shore A)	30 $\pm$ 0	41 $\pm$ 0	55 $\pm$ 0	66 $\pm$ 0	78 $\pm$ 0	84 $\pm$ 0
Compression set (%)	45 $\pm$ 1	52 $\pm$ 1	54 $\pm$ 1	55 $\pm$ 2	59 $\pm$ 2	53 $\pm$ 1
Resilience (%)	61 $\pm$ 0	54 $\pm$ 1	45 $\pm$ 1	38 $\pm$ 2	30 $\pm$ 1	28 $\pm$ 1
Abrasion (mm <sup>3</sup> )	136	58	40	29	37	36
Property change, after thermal aged 70°C at 96 h						
Tensile Modulus at 200% ( $\times 10^5$ Pa)	+2	+5	+11	+19	+27	N/A
Tensile strength (MPa)	-2	-1	+1	0	-2	-1
Elongation at break (%)	-271	-206	-118	-105	-103	-66
Tear strength (kN/m)	+2	+7	-3	-28	+1	-2
Hardness (Shore A)	+2	+2	+2	+3	+3	+3

N/A indicates not obtainable due to pre-mature fracture, and positive (+) and negative (-) values mean increase and decrease as compared with non-aged samples, respectively.

UV-B Neon Fluorescence Lamps emitting spectrum at a wavelength of 313 nm with Cycle 3 at 2 steps. The first step was UV exposure at 70°C for 8 h, and the second step was water condensation at 50°C for 4 h for the total time of 96 h. It should be noted that all the samples were kept and UV-degraded in the UV

apparatus at the same time, the samples being taken out periodically at required UV exposure times for further characterizations. The changes in mechanical properties were monitored before and after the UV and water condensation, the reported results being averaged by at least five determinations.

**TABLE III**  
**Cure Time, Mooney Viscosity and Mechanical Properties of Solid NR/SBR Vulcanizates for Different Concentrations of Precipitated Silica**

Properties	Silica content (phr)				
	0	10	20	30	40
Cure time (min : sec)	9 : 3	9 : 2	7 : 6	8 : 3	11 : 2
Mooney viscosity, ML (1 + 4) 100°C	19	18	24	39	94
Property, original					
Tensile modulus at 200% ( $\times 10^5$ Pa)	8 $\pm$ 0	10 $\pm$ 0	13 $\pm$ 0	28 $\pm$ 0	23 $\pm$ 0
Tensile strength (MPa)	8 $\pm$ 0	9 $\pm$ 1	11 $\pm$ 1	14 $\pm$ 1	17 $\pm$ 1
Elongation at break (%)	1099 $\pm$ 23	968 $\pm$ 30	921 $\pm$ 38	866 $\pm$ 35	880 $\pm$ 28
Tear strength (kN/m)	15 $\pm$ 1	14 $\pm$ 1	19 $\pm$ 1	26 $\pm$ 1	39 $\pm$ 0
Hardness (shore A)	30 $\pm$ 0	34 $\pm$ 0	42 $\pm$ 0	59 $\pm$ 0	57 $\pm$ 0
Compression set (%)	45 $\pm$ 1	51 $\pm$ 1	62 $\pm$ 1	69 $\pm$ 0	65 $\pm$ 2
Resilience (%)	61 $\pm$ 0	67 $\pm$ 0	64 $\pm$ 0	69 $\pm$ 0	65 $\pm$ 2
Abrasion (mm <sup>3</sup> )	136	29	29	116	86
Property change, after thermal aged 70°C at 96 h					
Tensile modulus at 200% ( $\times 10^5$ Pa)	+2	+6	+5	+6	+8
Tensile strength (MPa)	-2	+2	+3	+1	0
Elongation at break (%)	-271	-243	-101	-101	-180
Tear strength (kN/m)	+2	+13	+11	+4	0
Hardness (shore A)	+2	+5	+3	+5	+4

Positive (+) and negative (-) values mean increase and decrease as compared with non-aged samples, respectively.

**TABLE IV**  
Cure Time, Mooney Viscosity and Mechanical Properties of Solid NR/SBR Vulcanizates for Different Concentrations of Silica in FA

Properties	Silica in FA content (phr)				
	0	10	20	30	40
Cure time (min : sec)	9 : 3	11 : 0	10 : 1	10 : 0	10 : 3
Mooney viscosity, ML (1 + 4) 100°C	19	19	21	30	29
Property, original					
Tensile modulus at 200% ( $\times 10^5$ Pa)	8 $\pm$ 0	10 $\pm$ 0	13 $\pm$ 0	14 $\pm$ 0	16 $\pm$ 0
Tensile strength (MPa)	8 $\pm$ 0	6 $\pm$ 0	6 $\pm$ 1	7 $\pm$ 0	6 $\pm$ 0
Elongation at break (%)	1099 $\pm$ 23	878 $\pm$ 34	766 $\pm$ 37	816 $\pm$ 16	686 $\pm$ 18
Tear strength (kN/m)	15 $\pm$ 1	14 $\pm$ 1	15 $\pm$ 1	15 $\pm$ 1	15 $\pm$ 1
Hardness (shore A)	30 $\pm$ 0	33 $\pm$ 0	40 $\pm$ 0	45 $\pm$ 0	49 $\pm$ 0
Compression set (%)	45 $\pm$ 1	48 $\pm$ 1	49 $\pm$ 1	52 $\pm$ 3	52 $\pm$ 1
Resiliency (%)	61 $\pm$ 0	72 $\pm$ 1	71 $\pm$ 0	70 $\pm$ 0	65 $\pm$ 1
Abrasion (mm <sup>3</sup> )	136	116	112	91	92
Property change, after thermal aged 70°C at 96 h					
Tensile modulus at 200% ( $\times 10^5$ Pa)	+2	+2	+1	+4	+4
Tensile strength (MPa)	-2	+3	+1	-1	-1
Elongation at break (%)	-271	-46	-28	-184	-186
Tear strength (kN/m)	+2	+4	+4	+5	+5
Hardness (shore A)	+2	+4	+2	+3	+2

Positive (+) and negative (-) values mean increase and decrease as compared with non-aged samples, respectively.

## SEM studies

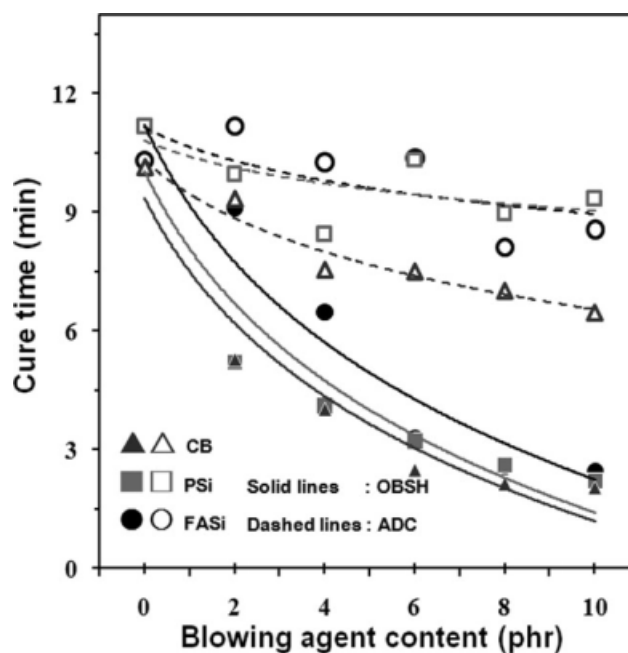
The foam structures and distributions of NR/SBR samples prepared by razor cut surfaces were viewed using a JEOL (JSM-5800LV) Scanning Electron Microscope (SEM) at 10 kV accelerating voltage.

## RESULTS AND DISCUSSION

### Solid NR/SBR blend vulcanizates

This part was studied to seek the optimum concentrations for CB, precipitated silica (PSi), and silica from FA (FASi) using solid NR/SBR blend ratio of 1 : 1. These optimum concentrations of the three fillers will then be used when examining the properties of cellular NR/SBR blend vulcanizates. Tables II-IV show the effect of filler content on the cure and mechanical properties of solid NR/SBR vulcanizates for CB (0-100 phr), PSi (0-40 phr), and FASi (0-40 phr) fillers, respectively. For all fillers, the Mooney viscosities appeared to increase with increasing filler contents, the effect being less pronounced for FASi filler. This was expected because the FASi particles were larger in size and had smaller surface area and a weaker filler-filler interaction as compared with the PSi particles. Cure times in all cases slightly changed within 1-2 minutes. In terms of mechanical properties (especially the tensile and tear strengths) and their changes after thermal ageing, it was found that the optimum filler content to be added in the NR/SBR vulcanizates for CB were 40-60 phr

whereas that for PSi and FASi were 40 and 30-40 phr, respectively. At the optimum concentrations of the three fillers, CB yielded the best reinforcing performance, especially for the tensile and tear strengths as expected. However, the compression set for the FASi filled NR/SBR vulcanizates was better than that for CB- and PSi-filled vulcanizates. This



**Figure 1** Effect of blowing agent content on cure time for NR/SBR vulcanizates filled with CB, PSi, or FASi (Solid line: OBSH and Dashed line: ADC).

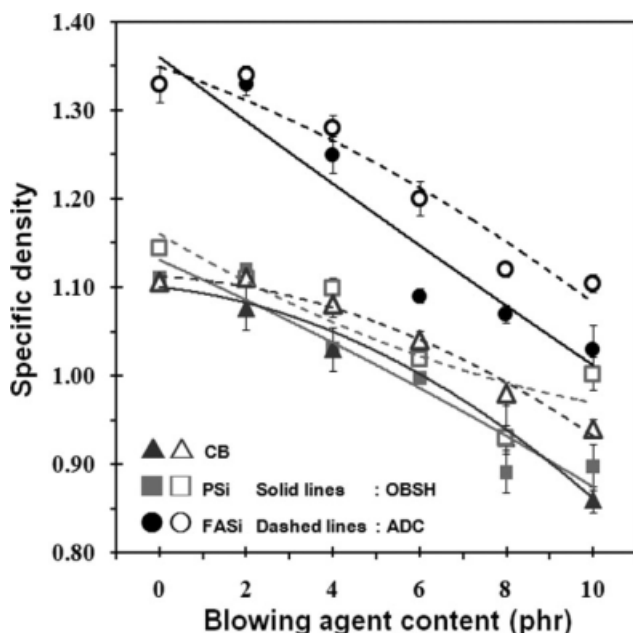


Figure 2 Specific density for NR/SBR vulcanizates filled with CB, PSi, or FASi as a function of blowing agent loading (Solid line: OBSH and Dashed line: ADC).

finding was in line with our previous work<sup>11</sup> stating the improved elastic properties of the NR/SBR blend through use of FA particles as extending filler.

It should be noted that the results in Tables II–IV were given in order to select the optimum contents of the three fillers used in solid NR/SBR vulcanizates, and therefore, the discussion to the results were not fully given due to that this work focused on the properties of the cellular NR/SBR blend vulcanizates.

**Cellular NR/SBR vulcanizates**

**Cure time properties**

In this section, fixed filler loading at 40 phr for CB, PSi, and FASi fillers was used for property comparison purposes in cellular NR/SBR vulcanizates, which were added with different concentrations of two chemical blowing agents (OBSH and ADC). Figure 1 shows the effect of blowing agent contents on cure time of NR/SBR blend vulcanizates for OBSH and ADC. It was found that the cure time decreased with increasing blowing agent content. This was because the blowing agents used exhibited exothermic phenomenon when decomposed within the rubber blend structure.<sup>13,14</sup> This suggested that there was an additional heat occurring in the rubber compound during the vulcanization process, and this would probably accelerate the crosslinking reaction,

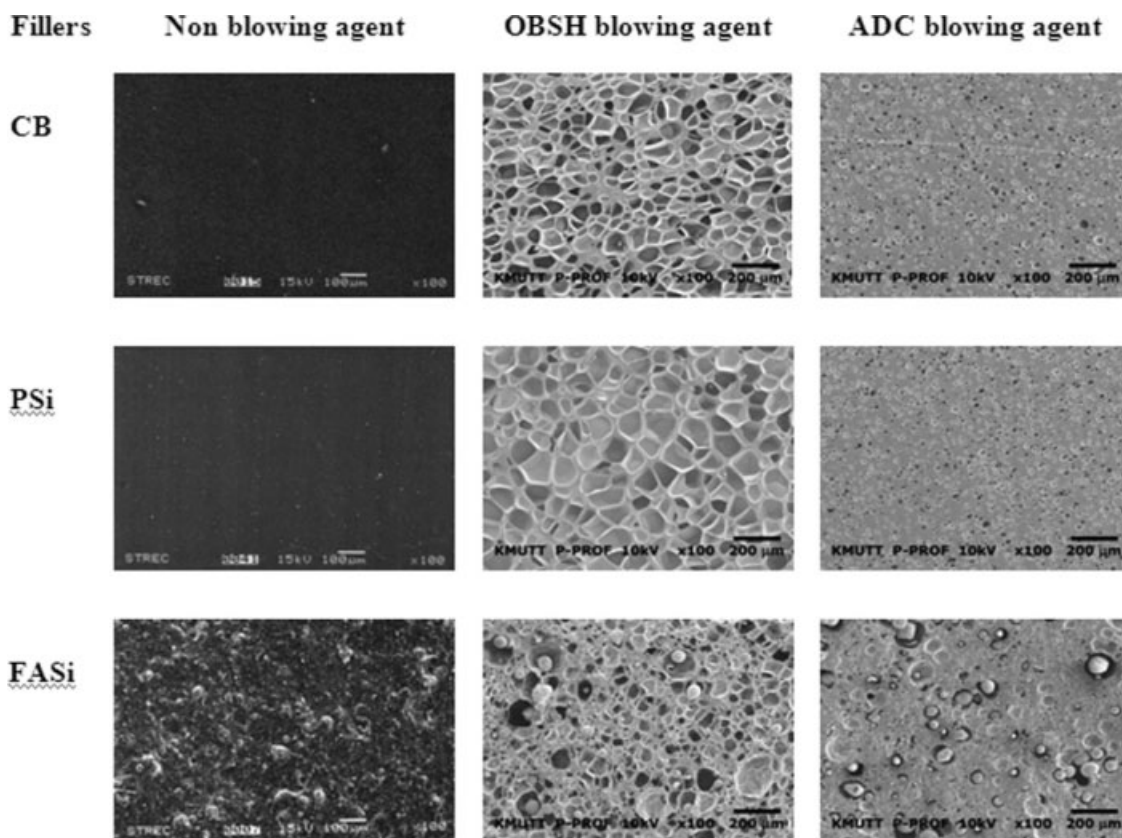
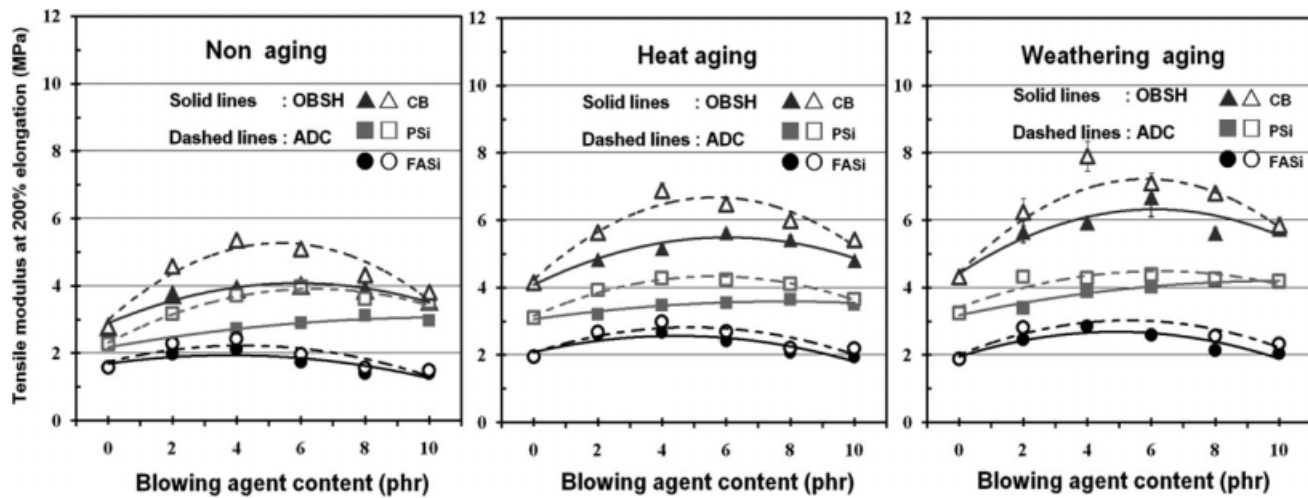


Figure 3 SEM micrographs for NR/SBR vulcanizates with CB, PSi, or FASi using with and without OBSH or ADC blowing agent at 6 phr (×100).

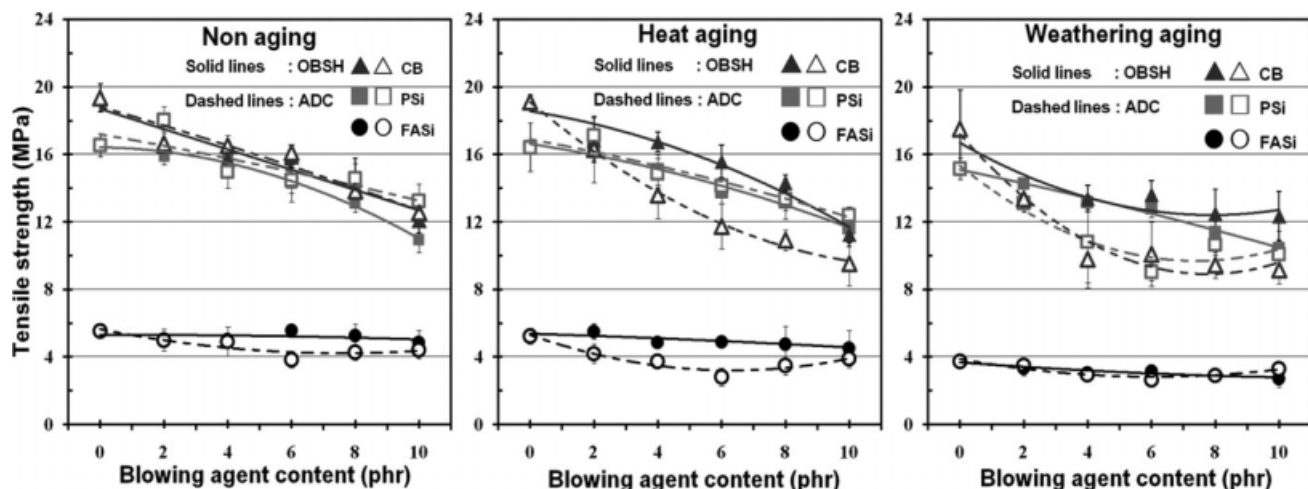


**Figure 4** Effects of OBSH and ADC contents and ageing on tensile modulus at 200% elongation for NR/SBR vulcanizates filled with CB, PSi, or FASi.

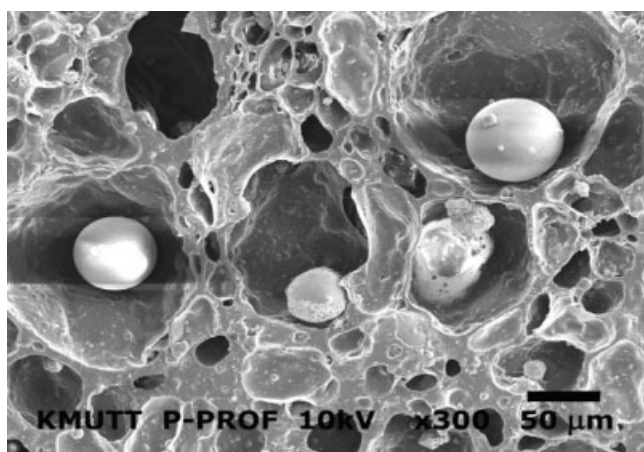
and thus reduced the cure time. It was also observed that the ADC agent showed a lesser drop in the cure time than the OBSH; i.e., the vulcanizates with OBSH had a faster curing than those with ADC. It was evident<sup>15</sup> that ADC agent could consume the zinc oxide acting as the activator in the rubber formulations to achieve a complete decomposition. If this was the case, the amount of zinc oxide for the crosslinking reaction of the vulcanizates with ADC agent would reduce as compared with OBSH agent and this caused the slower curing. When considering the effect of filler type, it was found that the cure time for CB filled NR/SBR vulcanizates had the lowest cure time as compared to that for PSi and FASi filled vulcanizates, this being very obvious for ADC case. This was because the CB itself is slightly alkaline (pH of around 7–8) with low oxygen content, and this may have an acceleration effect on the vulcanization reaction.<sup>16,17</sup>

#### Specific density and morphology

Specific density is one of the important characteristics and is related to cell structure and the overall weight of the foamed products. Figure 2 shows the specific density of the cellular NR/SBR vulcanizates with ADC and OBSH agents. It was noticeable that the specific density gradually decreased with increasing OBSH and ADC contents as expected due to production of gas phases in the rubber blend structure. The vulcanizates with FASi filler had the highest specific density. This can be explained by bulk densities of the three fillers used. The density of FASi has been reported to be around  $2.2 \text{ g/cm}^3$  whereas those of CB and silica are approximately  $1.8$  and  $1.9 \text{ g/cm}^3$ , respectively.<sup>18</sup> The NR/SBR vulcanizates with OBSH agent had slightly lower density than those with ADC, this being the case for all fillers used. This could be explained using the scanning



**Figure 5** Effects of OBSH and ADC contents and ageing on tensile strength for NR/SBR vulcanizates filled with CB, PSi, or FASi.



**Figure 6** SEM micrographs for FASi filled NR/SBR vulcanizates with OBSH blowing agent at 6 phr, displaying bubble coalescence around FA particle ( $\times 300$ ).

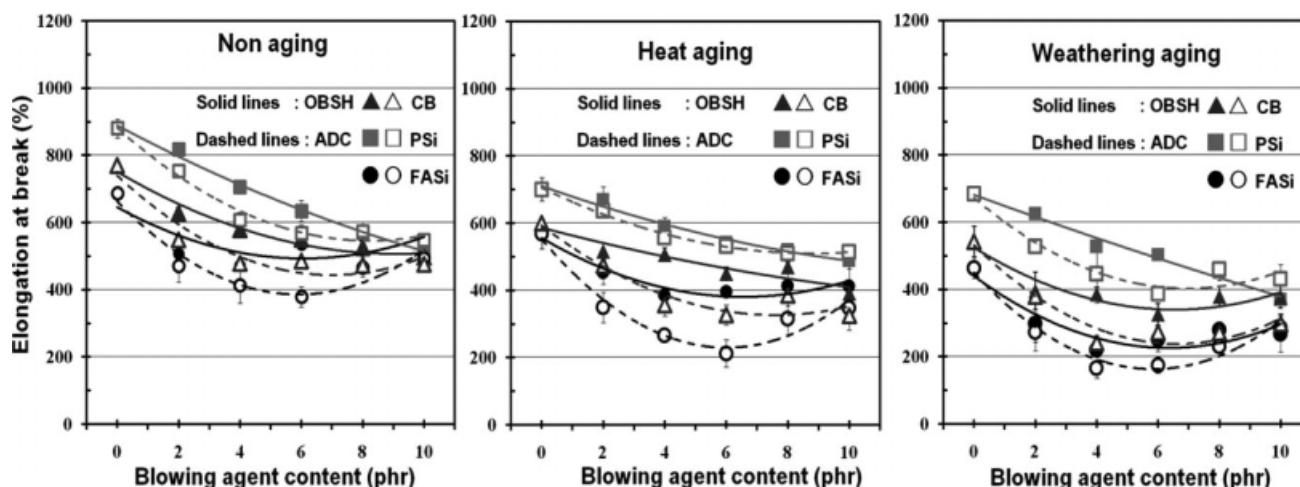
electron micrographs shown in Figure 3. It was found that the NR/SBR vulcanized foams produced by OBSH and ADC agents in this work had closed-cell structures. The vulcanizates with OBSH agent has greater size of foam cells as compared to those with ADC agent. The greater cell size by OBSH resulted from better dispersion and faster decomposition to produce gas phases of the OBSH as compared to ADC in the rubber matrix. This view was supported by Annicelli and Dick.<sup>15</sup> Figure 3 also shows that the cell sizes of the vulcanizates by the OBSH were relatively smaller than those by ADC, this being in good agreement with previous work by Sombatsompop and Lertkamolsin.<sup>2</sup>

**Mechanical properties and heat-weathering ageing**

Figure 4 shows tensile modulus at 200% elongation for the cellular NR/SBR vulcanizates reinforced by

CB, PSi, and FASi before and after heat and weathering ageing. In non-aged samples, the tensile modulus of the foamed vulcanizates increased with increasing blowing agent contents up to 6 phr and started to drop at higher loadings, except for the PSi filler. The increases in tensile modulus by the presence of the blowing agents were associated with closed-cell structures of the vulcanizates<sup>19</sup> whereas the decreases in the modulus at higher blowing agent loadings were due to gas containment limit.<sup>20</sup> For a given blowing agent content, the foamed vulcanizates with OBSH had lower tensile modulus than those with ADC due to greater number of foam cells in the NR/SBR structures as mentioned earlier. When considering the effect of filler type, CB gave the vulcanizates with highest tensile modulus due to the reinforcement effect and rigidity of CB.<sup>6</sup> After heat and weathering conditions, the tensile moduli for the foamed vulcanizates with all three fillers tended to increase due to increases in crosslink densities in the vulcanizates as a result of a post-curing effect.<sup>11</sup> The effect of thermal and weathering conditions seemed to be more pronounced in the NR/SBR vulcanizates with CB. This may be due to that the chemical interaction between CB and the rubber molecules were more sensitive to the crosslinking process.<sup>1</sup>

Figure 5 shows the effect of blowing agent content of OBSH and ADC on tensile strength of filled NR/SBR vulcanizates before and after heat and weathering ageing. It can be seen that the tensile strengths of CB and PSi filled NR/SBR vulcanizates for all blowing agent contents were much higher than those of FASi filled NR/SBR vulcanizates. This could be explained by the particle size and adhesion effects. As already stated in Experimental section, the particle size of the FASi was the largest and this would attribute to lower surface area for molecular



**Figure 7** Effects of OBSH and ADC contents and ageing on elongation at break for NR/SBR vulcanizates filled with CB, PSi, or FASi.



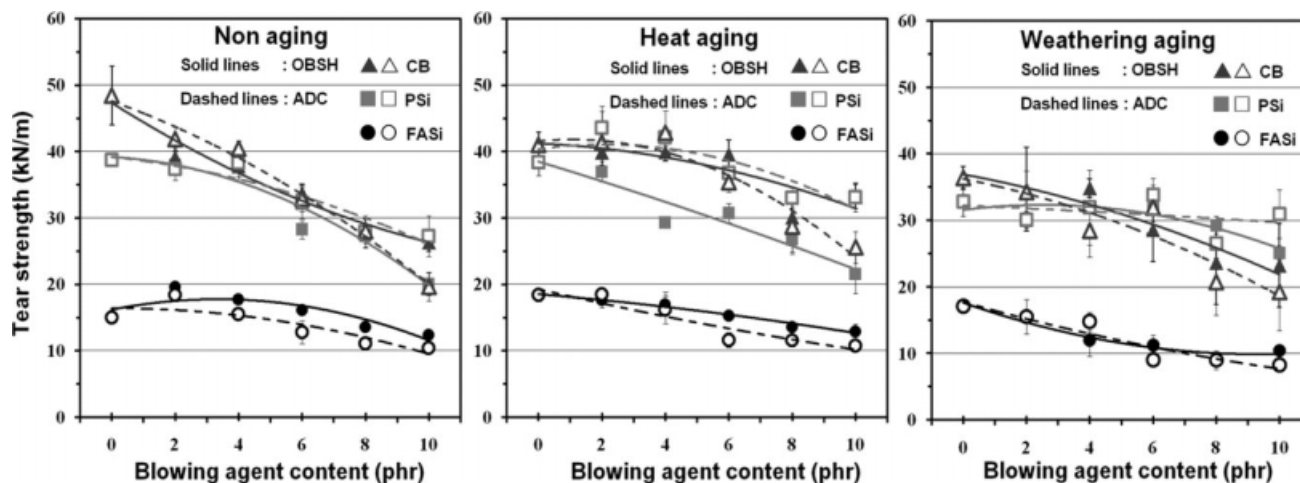


Figure 8 Tear strength for NR/SBR vulcanizates filled with CB, PSi, or FASi as a function of blowing agent loading.

interaction with the rubber although the FASi were chemically treated. In addition, it was evident in our previous work<sup>21</sup> that the FASi had broken into smaller pieces during the compounding process and these smaller pieces of the FASi filler were untreated during the filler surface treatment, and therefore resulted in particle aggregation and an increased filler-filler interaction. Another possible reason in the low tensile strength of the foamed vulcanizates with FASi was a coalescence of the gas phase around the ash particles shown in Figure 6. For the effect of blowing agent content, it was observed that the tensile strengths of CB and PSi filled NR/SBR vulcanizates decreased progressively with increasing blowing agent contents as expected because the rubber matrix phase to resist the tensile force had been reduced or replaced by the presence of gas phases. The higher the blowing agent content the greater the gas phases, and thus decreased tensile strength. After heat and weathering ageing, the tensile strength

slightly decreased. This may be due to two concurrent reactions of molecular degradation and crosslinking desulphuration, the latter reaction being referred to as a crosslink transformation from polysulphidic to mono or di-sulphidic crosslinks.<sup>1</sup> However, it was interesting to note that the effect of heat and weathering ageing was more sensitive and pronounced to the decrease in tensile strength for CB reinforced NR/SBR vulcanizates for ADC blowing agent system. This was postulated to be associated with the incomplete decomposition of the ADC during the initial crosslinking process, as compared to OBSH as mentioned earlier. Therefore, un-reacted (non-decomposed) ADC radicals may have resulted in further degradation of rubber molecules, and thus decreased tensile strength. The explanations for the changes in tensile strength in Figure 5 could also be used to describe the changes in elongation at break and tear strength in Figures 7 and 8, respectively.

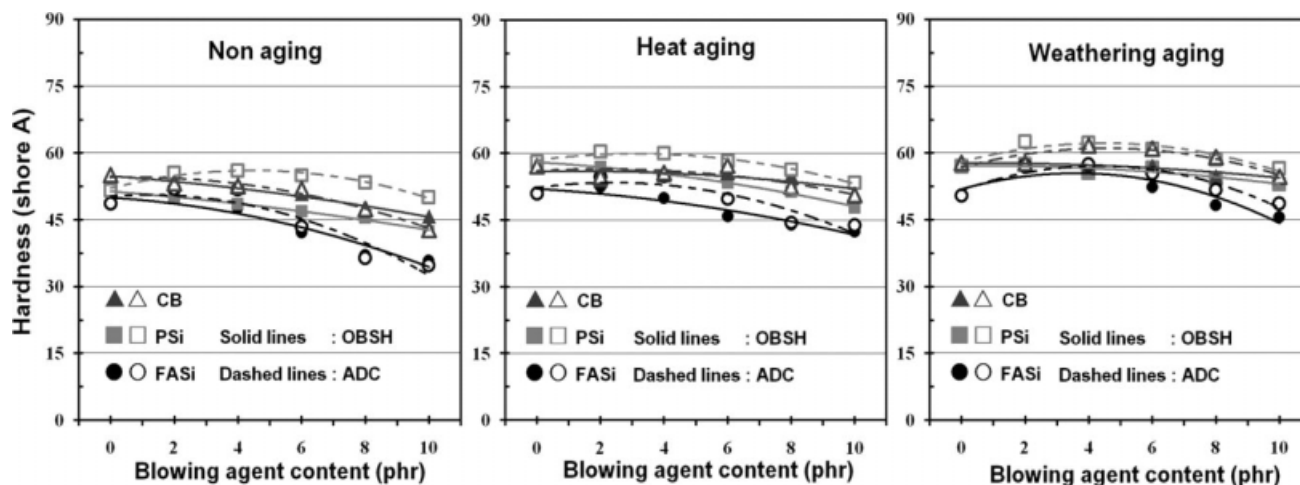


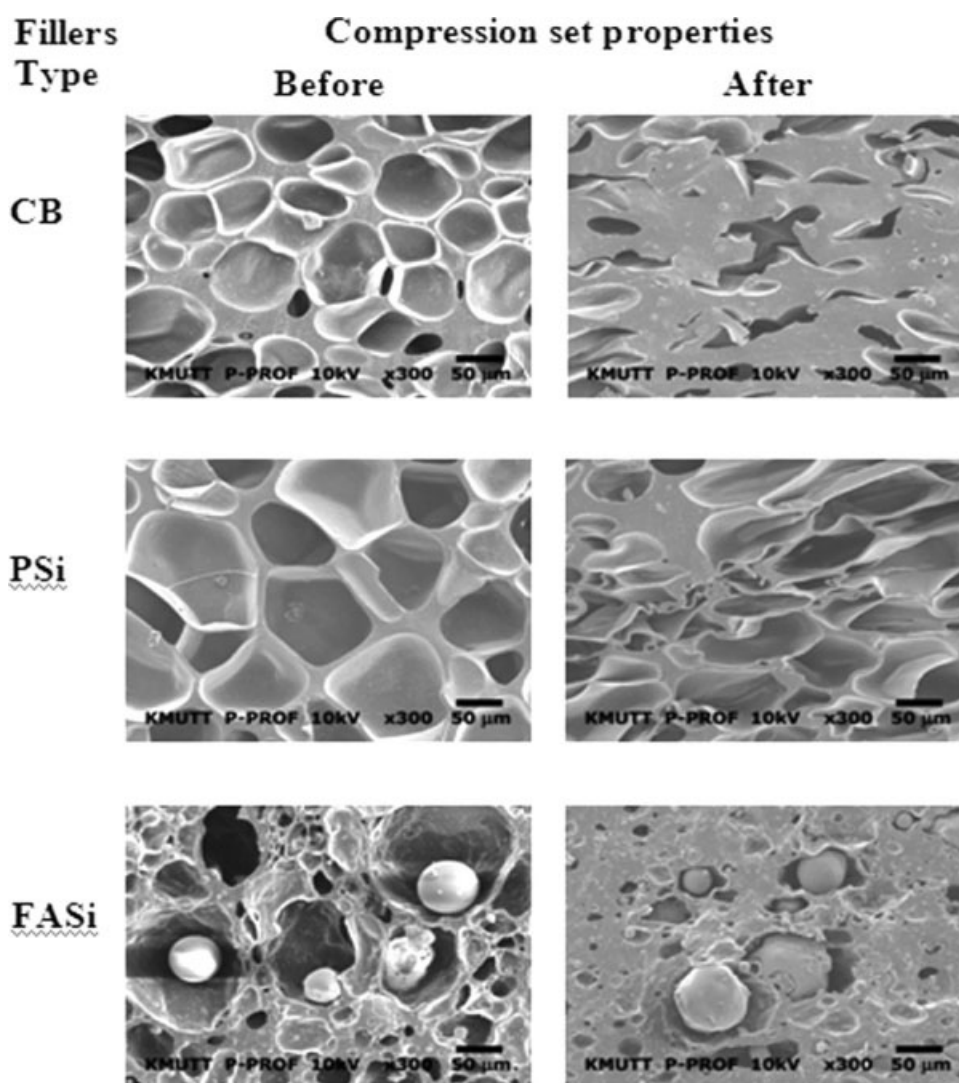
Figure 9 Effects of OBSH and ADC contents and ageing on hardness for NR/SBR vulcanizates filled with CB, PSi, or FASi.

**TABLE V**  
**Effects of OBSH and ADC Contents on Compression Set for NR/SBR Vulcanizates Filled with CB, PSi, or FASi**  
 (N/A: Could Not Be Molded)

Chemical blowing agent type	Fillers	Compression set (%)					
		Blowing agent content (phr)					
		0	2	4	6	8	10
OBSH	FA	52.3	50.2	56.4	66.0	N/A	N/A
	Silica	58.4	76.0	72.7	74.4	N/A	N/A
	CB	53.5	56.4	69.0	69.8	N/A	N/A
ADC	FA	52.3	52.6	59.9	63.9	N/A	N/A
	Silica	58.4	72.5	75.1	80.8	80.9	78.3
	CB	53.5	52.0	55.1	56.1	56.2	58.0

Figure 9 shows hardness results of the cellular NR/SBR vulcanizates as a function of blowing agent content. The trend and the explanations to the hardness results were very similar to those of the tensile modulus for both non-aged and aged rubber foams.

A slight difference in the modulus and hardness results was caused by the fact that the hardness measured the rigidity at the surface (solid) whereas the modulus had taken account the stiffness of the whole sample (solid and gas phases).<sup>22</sup>



**Figure 10** SEM micrograph of the foamed NR/SBR samples with 6phr OBSH before and after compression set testing.

**TABLE VI**  
Effects of OBSH and ADC Contents on Resilience for NR/SBR Vulcanizates Filled with CB, PSi, or FASi

Chemical blowing agent type	Fillers	Resilience (%)					
		Blowing agent content (phr)					
		0	2	4	6	8	10
OBSH	FA	65.2	62.8	64.1	63.3	63.4	63.2
	Silica	55.5	56.5	61.3	61.7	65.5	64.0
	CB	45.0	60.5	62.1	64.3	64.7	63.3
ADC	FA	65.2	72.4	74.7	68.8	65.9	63.6
	Silica	55.5	58.9	61.9	62.6	60.3	60.8
	CB	45.0	63.8	66.3	65.1	63.9	63.2

#### Elastic response of cellular NR/SBR

Table V shows effects of OBSH and ADC loadings on compression set for NR/SBR foamed vulcanizates loaded with CB, PSi, or FASi filler. As mentioned in the Experimental section that the vulcanizate sample used for assessing the compression set was cylindrical and had a diameter of 29 mm with 12.5 mm thick. With this sample configuration, there was a limit for OBSH loadings at 6 phr in all fillers and for ADC loadings at 6 phr only for FASi filler to obtain the foamed vulcanizates. Above these loadings, the foam samples could not be moulded. Considering the effect of filler type in OBSH system, it was found that the lowest compression, which corresponded to the best elastic recovery, was obtained by FASi filler whereas the poorest elastic recovery was given by PSi filler, especially at low blowing agent contents. For the ADC system, the FASi and CB exhibited similar compression set properties. Increasing the OBSH and ADC loadings reduced the elastic recovery. The decreases in elastic recovery of the NR/SBR vulcanizates could be explained using selected SEM micrographs (at 6 phr OBSH) as shown in Figure 10 which suggested that, after compression set testing there was a bubble-collapse or a breaking of the cell structures. This resulted in gas diffusion through the cell walls and lost the abilities to recover. Figure 10 also indicates more severe bubble-collapses occurring in the case of PSi. Effects of OBSH and ADC loadings on resilience for NR/SBR vulcanizates with CB, PSi, or FASi filler are given in Table VI. It was interesting to note that the elastic properties of solid NR/SBR vulcanizates with FASi were much better than those with CB and PSi fillers, but when foamed, the resilience properties for all fillers were indifferent. It suggested that the magnitudes of resilience changes for the vulcanizates with CB and PSi were greater than those with FASi by the presence of closed-cell foam structures. This was the case because the number of gas phases (foam structures) in the vulcanizates with CB and PSi were relatively greater. Taking the compression set and resilience results, it was suggested that the optimum concen-

tration of OBSH and ADC to be used for NR/SBR vulcanizates for cushion and gasket applications were 4 phr.

#### CONCLUSIONS

The cure characteristics, mechanical, and morphological properties of filled NR/SBR vulcanizates were studied through the effects of additions of OBSH and ADC blowing agents at various concentrations. Closed-cell structures of NR/SBR blend were obtained in all cases. The OBSH was more effective in reducing the cure time of the NR/SBR vulcanizates than the ADC. The mechanical properties for NR/SBR vulcanizates with CB were higher than those with precipitated silica and silica-based FA particles. The specific density of the NR/SBR blend progressively decreased with increasing OBSH and ADC contents. Tensile modulus and hardness increased after experiencing thermal ageing and weathering whereas the tensile strength, ultimate elongation, and tear strength reduced slightly after experiencing the heat and weathering ageing. The optimum concentration of OBSH and ADC to be used for NR/SBR vulcanizates was 4 phr. The elastic recovery for cellular NR/SBR vulcanizates decreased with increasing OBSH and ADC contents. For a given blowing agent content, the elastic recovery with silica-based FA particles was better than with CB and precipitated silica. The resilience properties for cellular NR/SBR vulcanizates increased with increasing blowing agent content.

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