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Effects of Foaming Agents and Calcium Carbonate on Thermo-Mechanical Properties of Natural Rubber Foams

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Summary

Natural rubber foams were prepared from the vulcanization of natural rubber in a sulfur curing system at 396 K by a two roll mill with foaming agents; sodium bicarbonate ($NaHCO_3$) or N, N´-dinitrosopentamethylene tetramine (DNPT, $C_5H_{10}N_6O_2$), and with 0, 20, 40, and 60 phr calcium carbonate ($CaCO_3$) as a filler. The obtained natural rubber foams are lightweight, with good thermal and mechanical properties, suitable for thermal insulation, energy absorption, and structural uses. Both foaming agents added in the natural rubber, namely $NaHCO_3$ and DNPT, decomposed and released gases at the vulcanization temperature of 396 K to produce open and closed cell structures. Adding of 60 phr $CaCO_3$ filler particles into the natural rubber foams enhanced the mechanical and thermal properties as the ionic charges Ca^{2+} and CO_3^{2-} produced the interatomic bondings within the natural rubber foam matrix. The obtained natural rubber foam with the 60 phr $CaCO_3$ filler and with $NaHCO_3$ possessed the bulk density, compression set, and thermal conductivity of 240.5 kg/m^3, 32.60%, and 0.066 W/mK, respectively. The obtained natural rubber foam with the 60 phr $CaCO_3$ filler and with DNPT possessed the bulk density, compression set, and thermal conductivity of 219.0 kg/m^3, 11.30%, and 0.070 W/mK, respectively, temperatures above 800°C.

KEYWORDS:
calcium carbonate filler
compression set
foaming agents
natural rubber foams
thermal conductivity

KLJUČNE RIJEČI:
pjene od prirodnog kaučuka
pjenila
punilo kalcijeva karbonata
toplinska provodnost
zaostala pritisna deformacija

Učinak pjenila i kalcijeva karbonata na termomehanička svojstva pjena od prirodnog kaučuka

Sažetak

Pjene od prirodnog kaučuka pripremljene su umrežavanjem prirodnog kaučuka u sustavu sumpornog umrežavanja pri 396 K s pomoću dvovaljčanog mlina s pjenilima: natrijev bikarbonatom ($NaHCO_3$) ili N, N´-dinitrosopentametilen tetraminom (DNPT, $C_5H_{10}N_6O_2$), te s 0, 20, 40 i 60 phr kalcijeva karbonata ($CaCO_3$) kao punilom. Dobivene pjene od prirodnog kaučuka su lagane, dobrih toplinskih i mehaničkih svojstava, prikladne za toplinsku izolaciju, apsorpciju energije i strukturne uporabe. Oba pjenila dodana u smjesu s prirodnim kaučukom, $NaHCO_3$ i DNPT, razgradila su se i oslobodila plinove pri temperaturi umrežavanja (umreživalištu) od 396 K, kako bi se stvorile otvorene i zatvorene stanične strukture. Dodavanje 60 phr $CaCO_3$ čestica punila u pjene prirodnog kaučuka poboljšalo je mehanička i toplinska svojstva kako su ionski naboji Ca^{2+} i CO_3^{2-} proizveli veze među atomima unutar matrice pjene prirodnog kaučuka. Dobivena pjena od prirodnog kaučuka s punilom 60 phr $CaCO_3$ i s $NaHCO_3$ imala je nasipnu gustoću od 240,5 kg/m^3, zaostalu pritisnu deformaciju od 32,60 % i toplinsku provodnost od 0,066 W/mK. Dobivena pjena od prirodnog kaučuka s punilom 60 phr $CaCO_3$ i s DNPT imala je nasipnu gustoću od 219,0 kg/m^3, zaostalu pritisnu deformaciju od 11,30 % i toplinsku provodnost od 0,070 W/mK, pri temperaturama iznad 800 °C.

Introduction

Cellular, sponge or cured expanded rubbers, called rubber foams, are widely used in three major applications: energy absorption, thermal insulation, and structural uses.[1] Cell structures of foams are composed of closed and open cell structures. The ability to perform various tasks mainly depends on the cell microstructure such as shape, size, and type, foaming agent used, density, and inorganic filler. The general ways to produce the foams are through the use of natural rubber latex in liquid form or a dry natural rubber in solid form. Chemical treatment is required for stabilizing the latex colloid; ammonia is normally added to stabilize and to affect the latex quality as the storage life and environmental impact aspects are improved. The rubber foams can be made from a dry natural rubber by compounding with a foaming agent and a vulcanizing agent providing cell expansion. The compounded rubber is simultaneously cured and foamed at various temperatures. Temperature is one of the important factors that affect foam properties: cell structure, density, and mechanical properties of based polymer. The higher temperature leads to a decrease in the overall crosslink density and an increase in the molecular mobility.

Blowing agents or foaming agents are an important substance in the vulcanization process to produce the natural rubber foams. N, N´ dinitrosopentamethylene tetramine (DNPT) and sodium bicarbonate ($NaHCO_3$) are two examples of common foaming agents used around the world. The role of rubber foaming agent is to generate inert gases within the rubber matrix as temperature increases and thermal decomposition occurs causing the cellular structure formation. Typical gases released from the foaming process are nitrogen gas (N_2), carbon monoxide gas (CO), and carbon dioxide gas (CO_2). Both temperature and time in the rubber vulcanization are also important processing parameters for the rubber foaming agents to produce different foam properties.[2-5]

In this work, the focuses are on using DNPT and $NaHCO_3$ as foaming agents because DNPT can generate nitrogen gas (N_2) having a molecular weight of 28 g/mol whereas $NaHCO_3$ releases carbon dioxide (CO_2)

having a molecular weight 44 g/mol, therefore yielding different physical, mechanical, and thermal properties. In particular, different molecular weights of the foaming agents cause different cell morphologies from the vulcanization process. In addition, there are many kinds of chemical substances used in rubber compounding such as zinc oxide (ZnO), stearic acid, sulfur (S), benzothiazyl-2-cyclohexyl-sulfenamide (CBS), and tetramethyl thiuram disulfide (TMTD) which are used as curing agents, cell reinforcing agents, cell nucleation agents, or cell stabilizers affecting the total gas released and the properties of natural rubber foams.[5-6] Other substances called additives or fillers are such as silica, carbon black, calcium carbonate, clay, and other oxide compounds are used primarily to provide foam mechanical reinforcement, and secondly to reduce cost.[7-9] Calcium carbonate ($CaCO_3$) is a very common filler in natural rubber and plastic industries to reduce production costs and to modify physical, mechanical and thermal properties of products due to the NR-$CaCO_3$ interaction.[10-12] The small filler particles with a higher specific surface area are expected to produce better mechanical properties.[13-18]

The goal of this work is to prepare and to evaluate the effects of foaming agents between sodium bicarbonate ($NaHCO_3$) and N, N´-dinitrosopentamethylene tetramine (DNPT, $C_5H_{10}N_6O_2$) and the effect of calcium carbonate ($CaCO_3$) added as a filler on mechanical, thermal, and physical properties of the natural rubber foams.

Experimental Part

Materials

The dry natural rubber (Standard Thai rubber 5L or STR 5L) was supplied by Venus Technology Co., Ltd (VTEC), Thailand. STR 5L has an extra light color and contains low dirt content (<0.04 wt%). The characteristics of STR 5L are good tensile properties, high compounded gum tensile strength, and low levels of non-polymer elements. The impurity content, the plasticity retention, the initial plasticity, and the Mooney viscosity (ML 1'+4', 100ºC) at 373 K of the STR 5L are equal to 0.02% by weight, 81.3, 32.0, and 62.8, respectively. The characteristics of STR 5L as determined according to SMR: Bulletin No. 7-1992 are shown in Table 1. The true density of the STR 5L as measured at room temperature is 920 kg/m^3 shown in Table 2.

Calcium carbonate ($CaCO_3$) (*Ajax Finechem Pty*. Ltd., Australia) was used as a filler. $CaCO_3$ has high purity (> 99 wt%) and with low impurity contents (< 1 wt%). The true density of $CaCO_3$ as measured at room temperature is shown in Table 2.

Sulfur (S), zinc oxide (ZnO), stearic acid, tetramethyl thiuram disulfide (TMTD), and benzothiazyl-2-cyclohexyl-sulfenamide (CBS) were provided from the Rubber Research Institute of Thailand, the Department of Agriculture of the Ministry of Agriculture, Bangkok, Thailand. The role of these chemicals is to act as the vulcanization agents for rubber compounds.

TABLE 2 – True density values of raw materials

Samples	True density, (kg/m^3)
STR 5L	920
$CaCO_3$	2,730

Titanium dioxide (TiO_2) has a brilliant white powdery appearance with high opacity was donated by the Rubber Research Institute of Thailand, the Department of Agriculture, the Ministry of Agriculture, Bangkok, Thailand.

Sodium bicarbonate ($NaHCO_3$) was provided from *Ajax Finechem Pty*. Ltd., Australia. The $NaHCO_3$ has high purity (>99.7 wt%), and with low impurity contents of Cl^-, PO_4^{3-}, S^{2-}, Ca^{2+}, Mg^+, Fe^{2+}, K^+, NH_4^+, Cu^{2+}, and Pb^{2+}.

N,N´-dinitrosopentamethylenetetramine (DNPT, $C_5H_{10}N_6O_2$) was donated by Nippon Zeon Co., Ltd., USA. DNPT has high purity (> 99.0 wt%). The molecular weight, density, temperature of decomposition in air, and temperature of resin and additive decomposition are equal to 0.186 kg/mol, 1,450-1,510 kg/m^3, 463-478 K, 403-463 K, respectively.

Natural Rubber Foams Preparation

The weight compositions of raw materials for natural rubber foams preparation are STR 5L, stearic acid, ZnO, TMTD, $NaHCO_3$, DNPT, CBS, TiO_2, and $CaCO_3$, all having the units in terms of parts per hundred rubber (phr), are shown in Table 3. The natural rubber foams were prepared from eight formulae which are classified by four formulae using $NaHCO_3$ as the foaming agent and the other four formulae by using DNPT as the foaming agent. The raw materials of natural rubber foams were fabricated by using a two-roll mill (*Mitsubishi*, model R11-3FF). The foaming agents or blowing agents ($NaHCO_3$ or DNPT) were added in proper weights. The natural rubber foams were vulcanized at 396 K for periods of time to obtain the optimum cure time (t_{90}), as identified from the rheometer cure curves.

Testing Methods

Cumulative mass percent finer and fractional distribution of calcium carbonate as a filler were determined by the particle size analyzer (*Model Polydisperse 2.19, Mastersizer S* long bed). Water was used as a medium phase to disperse calcium carbonate particles by an ultrasonic bath for 20 minutes before testing.

True density of samples was measured by a gas pycnometer (*Quantachrome, Ultra pycnometer 1000*) as the following Eq. 1:

$$\rho = \frac{Weight\left(D\right)}{True\ volume} \tag{1}$$

where ρ is the true density; D is the weight of dry sample (kg); and True volume is the volume of the solid component only. It was determined by

TABLE 1 – Quality of STR 5L according to SMR (Bulletin No. 7-1992)

Characterization	Results	*Bulletin No. 7-1992*
Dirt content (% by weight)	0.03	Part B.4
Volatile matters (% weight)	0.24	Part B.5
Ash contents (% by weight)	0.19	Part B.6
Nitrogen contents (% by weight)	0.32	Part B.7
Initial Plasticity (P_0)	27.0	Part B.8
Plasticity Retention Index (PRI)	51.9	Part B.8
Mooney viscosity ML (1´ + 4´) 373 K	75.2	Part B.9
Color	4.5	Part B.10

TABLE 3 – Composition of raw materials for natural rubber foam preparation

Raw materials/Formulae	1, (phr)	2 (phr)	3, (phr)	4, (phr)	5, (phr)	6, (phr)	7, (phr)	8, (phr)
STR 5L	100	100	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2	2	2
ZnO	4	4	4	4	4	4	4	4
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
$NaHCO_3$	5	5	5	5	-	-	-	-
DNPT	-	-	-	-	5	5	5	5
CBS	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
S	2	2	2	2	2	2	2	2
$CaCO_3$	0	20	40	60	0	20	40	60
TiO_2	5	5	5	5	5	5	5	5

phr = parts per hundred of rubber

crushing the piece into a powder form so that all pores are destroyed and by using the gas pycnometer method.[14]

Bulk density of samples was measured and calculated according to Eq. 2:

$$\rho = \frac{Weight(D)}{Apparent\ volume} \tag{2}$$

where ρ is the bulk density; D is the weight of dry sample (kg); and Apparent volume is the volume of sample including open pores and closed pored within the sample.[14]

Relative foam density of samples was measured and calculated according to ASTM D3575 and ASTM D1056 by using Eq.3 as given below;

$$\frac{Foam\ density\left({}^{kg}\!/_{m^3}\right)}{Solid\ density\left({}^{kg}\!/_{m^3}\right)} = Relative\ foam\ density \tag{3}$$

where Foam density is the density of natural rubber foam sample in terms of kg/m^3, and Solid density is the total density of solid raw materials used in making natural rubber foam in terms of kg/m^3.[14]

SEM photographs were captured by a scanning electron microscope (SEM, JEOL-5200) with the magnifications of 100 and 200 times and the acceleration voltages between 13-15 kV. The specimens of STR 5L, STR 5L/$CaCO_3$, and $CaCO_3$ powder were stacked on the stub by using a carbon paste and were coated with gold to obtain the conductive thickness of 0.1 µm.

X-ray diffraction (XRD) was taken by using a Bruker AXS analyzer (D8 Discover) with VANTEC-1 Detector. The specimens were examined by a double-crystal wide-angle goniometry and CuK_α radiation (λ = 0.15406 nm) with scanning angle (2θ) of 5 - 80° and scanning speed of 0.083° 2θ/s in 0.05 or 0.03° 2θ increments. The obtained characteristic peaks were matched with the *International Center for Diffraction Data Standard* (*JCPDS*) as reference patterns in order to confirm the crystalline phases.

The curing behavior was examined at 423 K by using an oscillating disc rheometer (*Techpro-Rheo Tech*, *ODR121105*, at *Rubber Research Center*, *Kasetsart University*, Thailand).

Crosslink density was determined at room temperature by using the toluene-swelling method (followed by *ASTM D-6814-02*). The vulcanized rubbers were cut into 0.0001 m^2 with 0.003-0.005 m thick and were weighed before and after equilibrium swelling in toluene for 72 hrs. The crosslink density was calculated by the Flory-Rehner equations 4 and 5:[14]

$$V_e = \frac{-\left[\ln\ln\left(1-V_r\right)+V_r+\chi_1 V_r^2\right]}{[V_1\left(V_r^{1/3} - {}^{(V_r)}\!/_{2)}\right]} \tag{4}$$

where υ_e is the efficient number of chains in the real network per unit volume (mol/m^3), V_r is the volume fraction at equilibrium within pure solvent of polymer in swollen network; the dimensionless χ_1 is the Flory-Huggins interaction parameter – polymer-solvent interaction– at 298 K (for toluene in cis-polyisoprene 0.391), and V_1 is the molecular volume of solvent (toluene 1.063x10^{-4} m^3/mol).[14]

$$V_r = \frac{(X_r / \rho_r)}{\left(\frac{X_r}{\rho_r}\right)+\left(\frac{X_s}{\rho_s}\right)} \tag{5}$$

where ρ_s is the density of toluene (g/cm^3), ρ_r is the density of raw rubber (g/cm^3), X_s is the mass fraction of toluene (g) obtained using Eq. (6), and X_r is the weight of rubber (g) as given by Eq.(7)

$$X_s = \frac{Weight\ of\ swollen\ sample(g) - Original\ weight(g)}{Weight\ of\ swollen\ sample(g)} \tag{6}$$

$$X_r = 1 - X_s \tag{7}$$

The compression set was determined through the ASTM D395-03 standard, Method B by using the compression set fixture (Hampden, APH40). The aim of compression set testing is to evaluate the ability of rubber compounds to maintain the elastic properties under compressive stress prolongation. The percentage of the original deflection is mainly related to the compression set, as follows:

$$C_B = [(t_o - t_i)/(t_o - t_n)] \text{ x } 100 \tag{8}$$

where C_B is the compression set, t_o is the original thickness of sample, t_i is the final thickness of the sample, and t_n is the thickness of the spacer bar.

Thermal conductivity of insulating rubber was measured at 297 K by using SS400 hard-chrome plating mold and followed by *ASTM C518*. The specimens were prepared in the square sheet 0.003 m^2 with 0.015 m thickness.

Results and Discussion

Physical Properties of Raw Materials and Natural Rubber Foams

The particle size distributions and cumulative mass percent finers (CMPF) of $CaCO_3$ as determined by the particle size analyzer are shown in Figure 1. The particle size distributions at CMPF 90% (d_{90}), CMPF 50% (d_{50}), CMPF 10% (d_{10}), and the average particle size (d_{avg}) of $CaCO_3$ powder are 57.79, 2.81, 0.67, and 20.50 micrometers, respectively. Poh et al. and Da, A.L.N, et al. reported that large calcium carbonate ($CaCO_3$) particles influenced inhomogenety, poor appearance, and inferior properties especially mechanical properties of natural rubber.[15-17] Therefore, adding the small $CaCO_3$ particles helps in mixing and dispersing other chemical substances and increases mechanical and thermal properties, consistent with the results reported by Sobhy, M.D. et al. and Tang, C.Y. et al.[18,19]

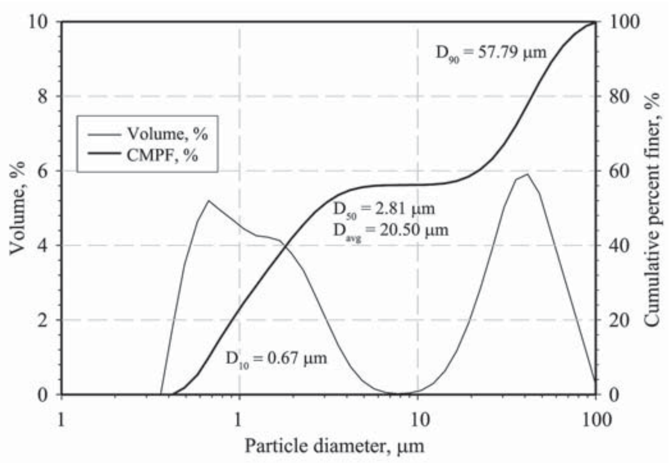

FIGURE 1 – Particle size distribution and cumulative mass percent finer of calcium carbonate

The bulk density and the relative density of natural rubber foams are tabulated in Table 4. The bulk densities of the first four formulae 1, 2, 3, and 4 with $NaHCO_3$ are equal to 225.8, 231.1, 239.5, and 240.5 kg/m^3, respectively. The bulk densities of the other four formulae 5, 6, 7, and 8 with DNPT are equal to 207.8**,** 215.0, 217.6, and 219.0 kg/m^3, respectively. As the amount of $CaCO_3$ filler particles added increases, the bulk density values of the natural rubber foams with $NaHCO_3$ and DNPT increase as well due to the interaction of NR-$CaCO_3$, consistent with the results reported by Sobhy, M.D. et al.[18] The type and quantity of gas outlet from the foaming agents also affect the open and closed cell morphology and the quantity of porosity per surface area. The relative foam density values of both foaming agents behave similarly to the bulk density values. As the amount of $CaCO_3$ filler particles increases, the relative foam density increases also.

The crosslink density of the natural rubber foams is tabulated in Table 5. The crosslink density values for both foaming agents ($NaHCO_3$ and DNPT) decrease monotonically as the amount of $CaCO_3$ particles increases due to the NR-$CaCO_3$ interaction, consistent with the results obtained by Sobhy, M. D.[18] and Kraus in Eq. 9.

$$\frac{\Phi_0}{\Phi_r} = 1 - \frac{mC}{1-C} \qquad (9)$$

where Φ_r and Φ_0 are the volume fractions of the filled rubber and gum vulcanizates respectively, and m is the rubber-filler interaction parameter that can be obtained from the slope.

The SEM micrographs of cross sectional areas of the pure natural rubber foams without $CaCO_3$ particles added, and natural rubber foams with $NaHCO_3$ and DNPT and with 60 phr $CaCO_3$, with magnifications of 100X and 200X, are illustrated in Figure 2. The SEM micrographs of the pure natural rubber foams with $NaHCO_3$ show the cell sizes to be bigger than those of the pure natural rubber foams with DNPT due to different gases released, namely CO_2 and N_2, as shown in Figures 2a, 2a-1, 2c and 2c-1. The generated and released gases, namely, nitrogen gas (N_2) from DNPT and carbon dioxide (CO_2) from $NaHCO_3$ possess different molecular weights, namely N_2 (28 g/mol) and CO_2 (44 g/mol).[2-4] Furthermore, adding $CaCO_3$ filler particles into the natural rubber foam matrix affected the cell morphology due to the ionic charges of Ca^{2+} and CO_3^{2-} providing the inter-atomic bonding within the matrix.[5,12] The calcium cation (Ca^{2+}) formed bonding within the natural rubber foams and altered mechanical and thermal properties whereas the carbonate anion (CO_3^{2-}) generated CO_2 gases during the vulcanization process. These caused the open and closed cell structures to be larger than those of the rubber foams without $CaCO_3$ added. Therefore, the natural rubber foams with $CaCO_3$ added with different foaming agents, namely $NaHCO_3$ and DNPT possess quite different pore sizes as shown in Figures 2b, 2b-1, 2d, and 2d-1. $NaHCO_3$ released CO_2 having a molecular weight higher than that N_2 released from DNPT. The molecular weight difference affected the cell structures of the fabricated natural rubber foams; the former cell sizes were larger.

The XRD peak patterns of natural rubber (STR 5L), $CaCO_3$ filler particles, the pure natural rubber foams with $NaHCO_3$ and DNPT, and the natural rubber foams with $NaHCO_3$ and DNPT and with 60 phr $CaCO_3$ added are shown in Figure 3. The XRD pattern of the STR 5L shows the amorphous phase whereas the XRD pattern of $CaCO_3$ particles shows the crystalline phase consistent with the JCPDS file numbers of 00-001-1032 and 00-003-0612, respectively. The latter indicates that calcium carbonate possesses the rhombohedral phase formation. The XRD peak patterns of

TABLE 4 – Bulk density and relative density values of natural rubber foams

Sample codes	Bulk density, kg/m^3	Relative foam density
Formula 1 STR 5L + $NaHCO_3$ + 0 phr $CaCO_3$	225.8 ± 2	0.245
Formula 2 STR 5L + $NaHCO_3$ +20phr $CaCO_3$	231.1 ± 1	0.251
Formula 3 STR 5L + $NaHCO_3$ +40phr $CaCO_3$	239.5 ± 2	0.260
Formula 4 STR 5L + $NaHCO_3$ +60phr $CaCO_3$	240.5 ± 3	0.261
Formula 5 STR 5L + DNPT + 0 phr $CaCO_3$	207.8 ± 2	0.226
Formula 6 STR 5L + DNPT+20phr $CaCO_3$	215.0 ± 1	0.233
Formula 7 STR 5L + DNPT+40phr $CaCO_3$	217.6 ± 1	0.237
Formula 8 STR 5L + DNPT+60phr $CaCO_3$	219.0 ± 1	0.238

TABLE 5 – Crosslink density and swelling ratio of the natural rubber foams

Samples	Crosslink density[a] (mol/m^3)	Swelling ratio[b]	Molecular weight, (M_c, kg/mol)[c]	Volume fraction of swollen polymer in solvent[d] (V_r)
Formula 1	151.75	2.07	2.15	0.32
Formula 2	95.50	4.76	9.72	0.17
Formula 3	82.00	5.16	11.26	0.16
Formula 4	74.28	5.44	12.41	0.15
Formula 5	184.83	1.71	5.00	0.75
Formula 6	135.25	3.99	7.07	0.19
Formula 7	103.05	4.57	9.04	0.15
Formula 8	70.81	5.58	12.99	0.17

[a] Crosslink density or effective number of chains in a real network per unit volume is calculated using the Flory-Rehner equation.
[b] Swelling ratio calculation; Swelling ratio = $(w_2-w_1)/w_1$, where w_1 and w_2 are the weight of swollen rubber and dry rubber, respectively.
[c] Average molecular weight between the network crosslinks
[d] Volume fraction of rubber in a swollen network in equilibrium with pure solvent (toluene)

the natural rubber foams with $NaHCO_3$ and DNPT and with 60 phr $CaCO_3$ added are of the semi-crystalline phases consistent with the JCPDS file numbers of 00-001-1032 and 00-003-0612 for STR 5L and calcium carbonate, and 00-003-0653 and 00-021-1119, for the foaming agents. The XRD patterns of the natural rubber foams show the semi-crystalline phase due to the amorphous phase of the natural rubber mixed with the crystalline phases of $CaCO_3$ and the foaming agents.

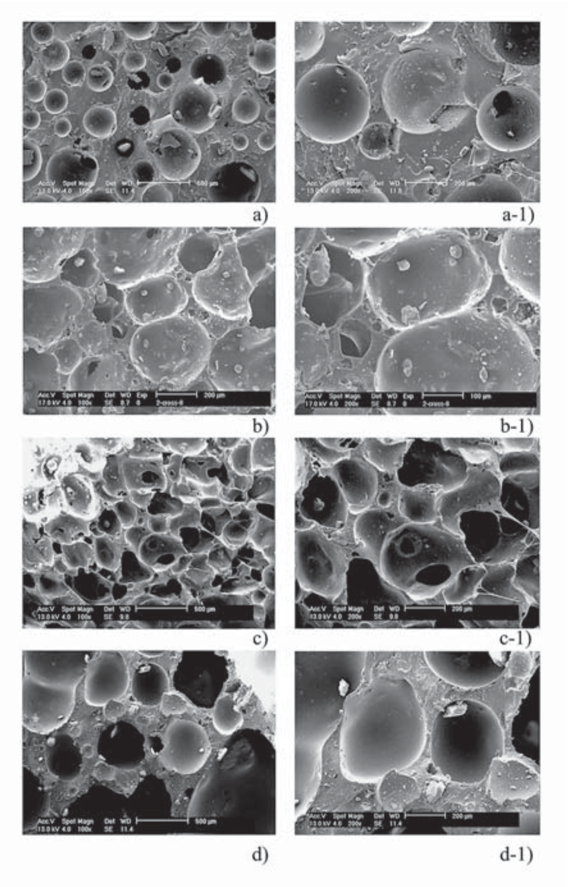

FIGURE 2 – SEM micrographs of cross sectional areas of pure natural rubber foams without $CaCO_3$ added and the natural rubber foams with $CaCO_3$ added at the magnifications of 100X and 200X, respectively; a) and a-1) the natural rubber foams with $NaHCO_3$ without $CaCO_3$ added; b) and b-1) the natural rubber foams with $NaHCO_3$ and with 60 phr $CaCO_3$ added; c) and c-1) the natural rubber foams with DNPT and without $CaCO_3$ added; d) and d-1) the natural rubber foams with DNPT and with 60 phr $CaCO_3$ added

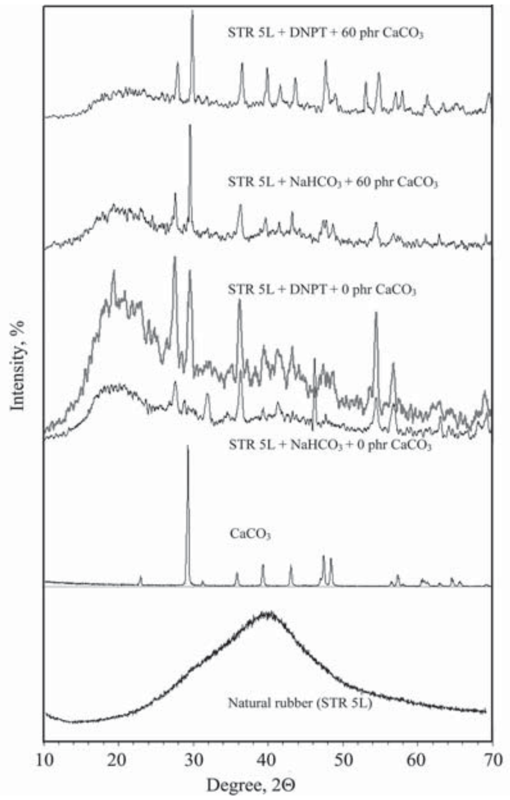

FIGURE 3 – XRD patterns of pure STR 5L, $CaCO_3$, natural rubber foams with $NaHCO_3$ and with 0 and 60 phr $CaCO_3$ added, and the natural rubber foams with DNPT and with 0 and 60 phr $CaCO_3$ added

Mechanical Properties of Natural Rubber Foams

The data of Mooney viscosity, curing time (t_{90}), and compression set of the composite natural rubber foams, measured according to the *ISO 289-1*, *ASTM D5289*, and *ASTM D 395-03 Method B*, respectively, are tabulated in Table 6. As the amount of $CaCO_3$ particles increases, both the Mooney viscosity and the optimum cure time t_{90} values decrease. The Mooney viscosity and optimum cure time of natural rubber foams without $CaCO_3$ added and with DNPT (Formula 5) decrease less drastically than those of the samples with $NaHCO_3$ (Formula 1) because the natural rubber foams with $NaHCO_3$ contain ionic bonding (Na^+, HCO_3^-) whereas the natural rubber foams with DNPT ($C_5H_{10}N_6O_2$) contain only covalent bonding within the natural rubber foam matrix. The covalent-covalent bonding with DNPT is easier to form than the ionic-covalent bonding with $NaHCO_3$. In general, the ionic bond is stronger than the covalent bond.[20] Therefore, the different foaming agents used and the bonding types occurred required different optimum cure times. The optimum cure time of natural rubber foams with $NaHCO_3$ and without $CaCO_3$ added was longer than that of the rubber foams with DNPT and without $CaCO_3$ added. However, when $CaCO_3$ was added into the rubber foams of both DNPT and $NaHCO_3$, the Mooney viscosity and optimum cure time values decreased DNPT due to the NR-$CaCO_3$ interaction, consistent with the results reported by Sobhy, M.S. et al. Summarized, the $CaCO_3$ filler added in the natural rubber foams with $NaHCO_3$ (Formulae 2, 3, 4) affected the Mooney viscosity and optimum cure time more drastically than those with DNPT (Formulae 6, 7, 8).

With increasing $CaCO_3$ content embedded into the natural rubber foams, the compression set value decreases as shown in Table 6, consistent with the results reported by Sobhy M.D. et al.[18] and Tang, C.Y. et al.[19] Furthermore, the compression set values of the natural rubber foams with the DNPT are lower than those of the natural rubber foams with $NaHCO_3$ due to the higher quantity and smaller sizes of closed and open cells per surface area, consistent with the SEM photographs as shown in Figure 2. Thus, different cell sizes and amounts of cell appear to critically affect the compression set values, as shown in Table 6. It can be noted that the compression set values are also consistent with the obtained crosslink density values. There are large deviations in the compression set values in the case of DNPT (Formulae 6, 7, 8). Therefore, both foaming agents ($NaHCO_3$ and DNPT) and $CaCO_3$ filler particles added in the natural rubber foam matrices are shown here to critically affect the Mooney viscosity, the t_{90}, and the compression set.

Thermal Properties of Raw Materials and Natural Rubber Foams

The differential scanning calorimeter (DSC) profiles, used to study the heat flow vs. the temperature from room temperature to 773 K, of both foaming agents ($NaHCO_3$ and DNPT) are shown in Figures 4a and 4b, respectively. The heat capacity values (C_p) of $NaHCO_3$ and DNPT are 6876.87 KJ/Kg.K at 435.71 K and 1575.21 KJ/Kg.K at 440.43 K, respectively.[21,22] The DSC results of $NaHCO_3$ and DNPT as foaming agents suggest that $NaHCO_3$ has a higher heat capacity value than that of DNPT. This means $NaHCO_3$ requires or adsorbs more energy than that of DNPT according to the thermal property theory.[20]

The specific heat of the natural rubber foam with 60 phr $CaCO_3$ added and with $NaHCO_3$ is shown in Figure 5a. The specific heat of the natural rubber foam with 60 phr $CaCO_3$ added and with DNPT is shown in Figure 5b. The mixture's rule of composite materials was used to calculate the upper and lower bounds, consistent with the results obtained by Tang, C.Y. et al.[20] Adding 60 phr $CaCO_3$ filler particles into the natural rubber foams with $NaHCO_3$ induced the higher specific heat value than that of the natural rubber foam with DNPT. This is because $NaHCO_3$ can absorb more heat than DNPT.

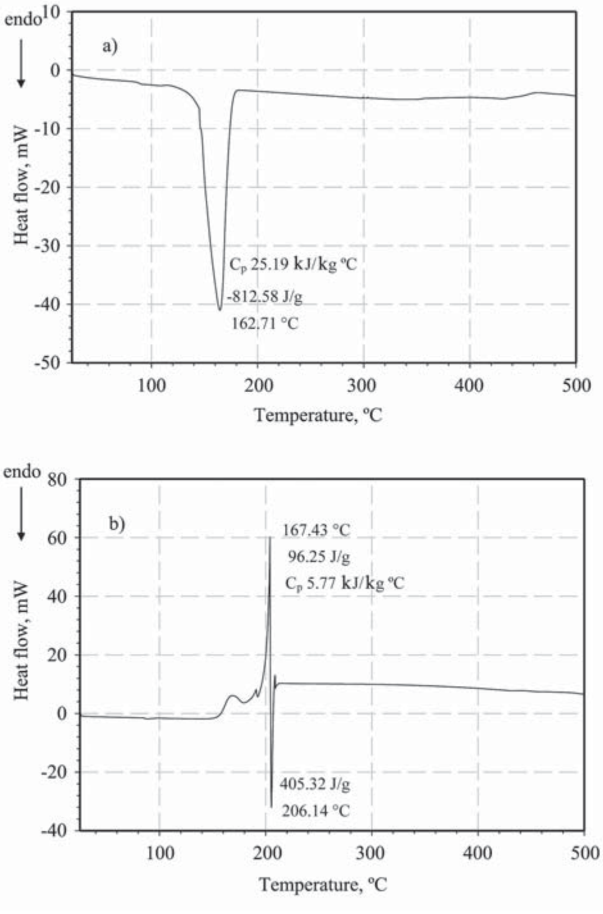

FIGURE 4 – DSC profiles of foaming agents: a) $NaHCO_3$; and b) DNPT

Thermal conductivity values of four natural rubber foams (Formulae 1, 4, 5, and 8) were measured according to the ASTM C518 and are tabulated in Table 7. The natural rubber foams with the foaming agents ($NaHCO_3$ and DNPT) but without $CaCO_3$ added have the thermal conductivity values of 0.068 and 0.049 W/m.K, respectively, depending on the cell size, the specific heat, and the heat capacity. The natural rubber foams with $NaHCO_3$ and DNPT and with 60 phr $CaCO_3$ added have the thermal conductivity values of 0.066 and 0.070 W/m.K, respectively. Adding

TABLE 6 – Mooney viscosity, optimum cure time, and mechanical properties of composite natural rubber foams

Properties/Formulae	Pure STR 5L	1	2	3	4	5	6	7	8
Mooney Viscosity (ML 1′ + 4′) 373 K *ISO 289-1*	31.8	24.0	15.40	14.30	13.30	13.20	12.94	12.00	10.30
t_{90} (min) Optimum cure time (MDR Type, *TECH PRO*) Arc 0.5°, 423 K *ASTM D 5289*	-	35.02	13.36	10.57	10.02	12.94	12.44	12.38	12.22
Compression set 343 K, 22 hr. (%) *ASTM D 395-03 (Method B)*	-	49.50	39.70	35.40	32.60	46.20	11.50	11.40	11.30

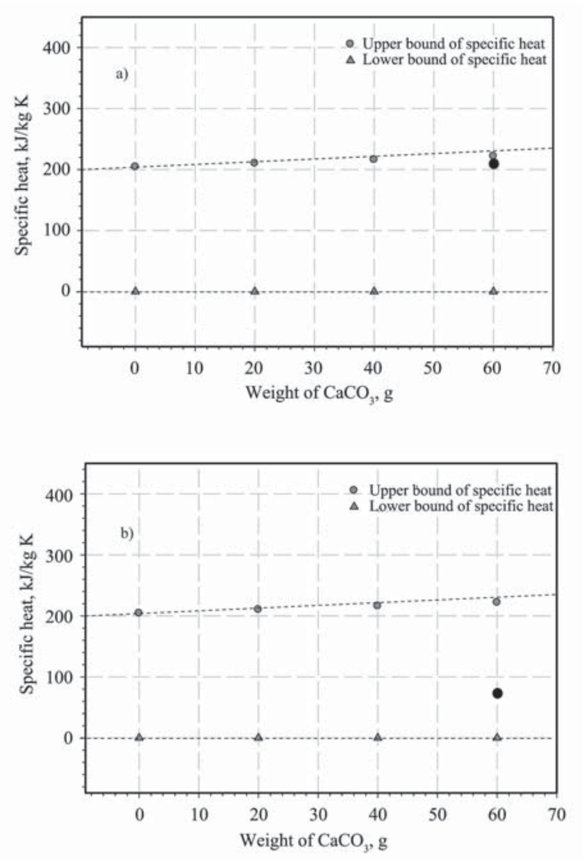

FIGURE 5 – a) specific heat of the composite natural rubber foams with 60 phr $CaCO_3$ added and with $NaHCO_3$, and b) specific heat of the composite natural rubber foams with 60 phr $CaCO_3$ added and with DNPT

$CaCO_3$ filler particles into the natural rubber foams affects the thermal conductivity value of the DNPT foam because $CaCO_3$ is an inorganic oxide material. In general, the oxide ceramic material possesses high melting temperatures and good thermal resistance. Therefore, $CaCO_3$ increases the thermal property of the natural rubber foams due to the ionic charges of Ca^{2+} and CO_3^{2-} which provide the inter-atomic bonding within the natural rubber foam matrix.

Conclusions

Sodium bicarbonate ($NaHCO_3$) and N, N´-dinitrosopenta methylenetetramine (DNPT) as the foaming agents are shown to produce the closed and open cell morphology during the vulcanization process to obtain the natural rubber foams.[2-6,22] $NaHCO_3$ and DNPT released CO_2 and N_2, respectively, during the vulcanization process.[3,22] The type of gas released critically affected cell size of various mechanical, thermal, and physical properties.[10,13,18] Furthermore, adding $CaCO_3$ filler particles into the natural rubber foams affected directly various mechanical properties, namely, the Mooney viscosity, curing time, and the compression set: thermal properties, namely, the thermal conductivity, heat capacity, and specific heat: and physical properties such as the bulk density, crosslink density, and relative foam density. Both foaming agents and the filler are shown here to critically influence the physical, mechanical, and thermal properties of the natural rubber foams fabricated. The rubber with 60 phr $CaCO_3$ added and with $NaHCO_3$ possessed the bulk density, relative foam density, crosslink density, compression set, and thermal conductivity values of 240.5 kg/m^3, 0.2614, 74.279 mol/m^3, 32.60%, and 0.066 W/m.K, respectively. The natural rubber foam with 60 phr $CaCO_3$ added and with DNPT possessed the bulk density, relative foam density, crosslink density, compression set, and thermal conductivity values of 219.0 kg/m^3, 0.2380, 70.808 mol/m^3, 11.30%, and 0.070 W/m.K, respectively. Both types of foaming agents are suitable foaming agents for producing the natural rubber foams. $CaCO_3$ is also suitable filler to enhance the mechanical properties and the thermal resistance of the natural rubber foams fabricated.

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TABLE 7 – Thermal conductivity values of composite natural rubber foams

Sample codes	Average thermal conductivity[a], W/m.K
Formula 1 STR 5L + $NaHCO_3$ + 0 phr $CaCO_3$	0.068
Formula 4 STR 5L + $NaHCO_3$ + 60 phr $CaCO_3$	0.066
Formula 5 STR 5L + DNPT + 0 phr $CaCO_3$	0.049
Formula 8 STR 5L + DNPT + 60 phr $CaCO_3$	0.070

[a] Three samples were measured and the average thermal conductivity value is tabulated for each formula.

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IZLOG KNJIGA

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Grundlagen und Anwendungen des Additive Manufacturing (AM)

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Sadržaj: *Vorwort, Grundbegriffe, Definitionen und Anwendungen; Schichtbauverfahren; Anwendungen; Additive Manufacturing, Konstruktion und Strategien; Materialien, Entwurf und Qualitatsaspekte für additive Herstellungsverfahren; Glossar; Literatur; Index.*

Danas je aditivna proizvodnja (AM) poznata u svim industrijama i postala je nezamjenjiv skup postupaka proizvodnje modela, prototipova, funkcionalnih tvorevina, kalupa i alata od plastike i metala. Dolaskom na tržište manjih i jeftinijih strojeva, sve više prevladava pojam 3D tiskanje. Knjiga je namijenjena svima koji žele znati više o AM postupcima: od znanstvene zajednice do industrije te učenika i studenata.

Od početaka postupaka poznatih pod nazivom brza izrada prototipova (e. *Rapid prototyping*, RP) osamdesetih godina prošloga stoljeća pa do danas, pod nazivom aditivna proizvodnja smatraju se proizvodni postupci u kojima se tvorevina izrađuje slaganjem sloj na sloj. Aditivni postupci označavaju istinsku revoluciju u postupcima praoblikovanja, stvaranja početnog oblika tvorevine, odnosno promjenu proizvodnih postupaka za velike serije istih tvorevina u proizvodnju različitih tvorevina malih serija.

U knjizi su, u pet poglavlja, prikazane karakteristike 3D tiskanja, ali i njihov utjecaj na ostale postupke prerade metala i plastike. Poglavlja su podijeljena na osnovne pojmove, definicije i primjenu, vrste aditivnih postupaka, njihovu primjenu u raznim industrijama, modeliranje i materijale. Na kraju knjige dan je rječnik s pojmovima i njihovo objašnjenje.

Prilika je da se upozori na različitost naziva ove revolucionarne skupine postupaka praoblikovanja u raznim jezicima. U engleskom je uobičajen naziv *Additive Manufacturing*, u njemačkom učestalo se rabi *Additive Fertigung*. Zašto je u hrvatskom prihvaćen izraz aditivna proizvodnja, što odgovara engleskom *additive production* (*fabrication*) ili u njemačkom *Additive Produktion*?

Polazeći od Ropohlove (1979.) razredbe tehničkih sustava prema klasi funkcije i pretežnom izlazu, riječ proizvodnja (proizvodna tehnika) je zajedničko ime za procesnu i izradbenu tehniku. To znači da su ekvivalenti na engleskom *production technology = processing technology + manufacturing technology*, a u njemačkom *Produktionstechnik = Verfahrenstechnik + Fertigungstechnik*. Postoji li potreba za takvom razlikovnošću? Postoji, jer u osnovi treba razlikovati dvije skupine postupaka aditivne proizvodnje.

Prvi postupak aditivne proizvodnje bila je stereolitografija 1987. U radnoj komori kapljevina (duromerna smola) s pomoću laserske zrake polimerizira i umrežuje.

Postoje i postupci aditivne izradbe. To su postupci nanošenja slojeva taljenjem plastomerne žice (akrilonitril/butadien/stiren, ABS) koji hlađenjem prelaze u čvrsto stanje, što je odlika izradbenih postupaka praoblikovanja.

Ana PILIPOVIĆ i Igor ČATIĆ