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Composites of natural rubber, carbon black, and kaolin sodium bicarbonate content for sponge application

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Abstract. Modification of rubber-carbon-kaolin composite with sodium bicarbonate into sponges was carried out through the process of mastication, vulcanization and printing. The main ingredients consisted of natural rubber, carbon black, kaolin and sodium hydrogen carbonate. The research methodology was based on the development of composite rubber-carbon-kaolin by varying the composition of fillers which were kaolin and Sodium Bicarbonate. The results showed that mechanical properties of the modified sponge rubber-carbon-kaolin composite with sodium hydrogen carbonate for the formula B (Kaolin: Calcium Carbonate = 8:38 phr) had specific gravity of 0.51 g/cm³, compression set of 28,05%, tensile strength of 34,46 N/m³ and elongation at break of 212%. Based on the morphological analysis (SEM micrographs), the porosity of the composites was not homogenous. In addition, based on the thermal gravimetric analysis (TGA) there was a decrease in relative mass due to the differences kaolin and Natrium Bicarbonate loading.

Keywords: carbon black; composite: modification; natural rubber; sponge

1. Introduction

Natural rubber (NR) with an empirical formula (C₅H₈)_n is an elastomer with a chemical structure of cis-1,4-polyisoprene with various advantages that can be applied to various types of engineering according to its designation [1-5]. The advantages of natural rubber are caused by their mechanical properties such as flexible, elastic, viscos which cannot be replaced by synthetic rubber [6]. The weaknesses of natural rubber, among others, are not resistant to friction, heat, and oil. Natural rubber has a double bond among molecules hence it has a higher tensile strength during strain [7].

NaHCO₃ was added to NR composites, carbon black (CB) and kaolin through the decomposition process and the carbon dioxide was released which was characterized by the formation of air cavities that formed foam. The foam formed was caused by carbon dioxide gas that resulted from the decomposition of NaHCO₃ [8].

Substances that played an active role as blowing agents or foaming agents in the vulcanization process and caused the formation of rubber foam was N, N "dinitrosopentamethylene tetramine (DNPT) and NaHCO₃ [9]. Najib *et al.* [10] reported that the difference in concentration of NaHCO₃ added to NR as a blowing agent affected the foam morphology and the number of foam cells per unit volume. The development of NR into sponge has been carried out by previous researchers mainly using materials from concentrated latex. Prompunjai and Sridach [11] developed a sponge from concentrated latex through a process of vulcanization with sulphur and peroxide to produce foam with an open cell structure. Zakaria *et al.* [12] reported the addition of NaHCO₃ as a blowing agent on 8 phr concentrations on ethylene rubber propylene diene monomer (EPDM) to decrease compression set along with the



increase of process temperature from 140°C, 150°C and 160°C. Tenebe *et al.* [13] conducted a study of CB N330 and luffa-aeqytiaca filler (LAF) as filler in the manufacture of sponges from natural rubber which could improve the mechanical properties of the sponge produced.

According to Shakir *et al.* [14] the addition of NaHCO₃ as a blowing agent on polyurethanes could release CO₂ by forming cell structures. Shakir *et al.* [14] reported the addition of NaHCO₃ to polyurethanes decreased tensile strength, modulus, elasticity, but could increase elongation. Tangboriboon *et al.* [15] reported the development of foam thermal insulation composite from NR with NaHCO₃ from dispersed eggshell at 150°C vulcanization temperature which produced foam rubber composites with mechanical properties such as compression sets, cross link density, bulk density, and relative foam densities 0.070 W/mK, 45.0%, 6.95 x 10⁻⁵mol/cm³, 0.58, and 0.63 respectively.

Vahidifar *et al.* [16] reported that an increase in CB concentrations in rubber foams of 0; 5; 10; 15; and 20 phr increased cell density, hardness, compression, modulus, number of cells with a smaller size. Furthermore, Pechurai *et al.* [17] reported an increase in concentrations of oxybis (benzene sulfonyl hydrazide (OBSH) (0; 3; 6; and 9) phr as a blowing agent which resulted in a decrease in hardness, and a fluctuation in the value of compression set. In addition, it was also reported that an increase in the CB ratio from 15 to 70 phr caused an increase in density, tear strength, and tensile strength, but conversely proportional to the decrease of elongation at break.

The development of NR into sponge in this study used Standard Indonesian Rubber/ Crumb Rubber SIR 20 rubber with CB, kaolin and CaCO₃ fillers. Meanwhile, blowing agents (NaHCO₃) and filler (Carbon Black and Kaolinite). CB and Kaolin were intended to be added to improve physical mechanical properties and increase the amount of air cavity of the sponges. According to Nayak *et al.* [18] the ratio of CB as a reinforcing ingredient to the sponges could inhibit the growth of the number of cells and the area of air cavity formed. The use of CaCO₃ as a filler to improve the mechanical properties of rubber finished goods has been widely used Deng *et al.* [19] and Song *et al.* [20]. Furthermore, Dalen *et al.* [21] stated that the addition of kaolin can increase curing rate, but the kaolin excess causes a reduction of foam. This study aims to observe the effect of kaolinite, Calcium Carbonates on the physical mechanical properties of rubber composites using NaHCO₃ as a foaming agent. In order to examine the surface area and its morphological characteristics, Scanning Electron Microscope (SEM) was conducted. In addition, thermal gravimetric analysis (TGA) was applied to study its thermal properties of the sponges.

2. Experimental Procedures

2.1. Materials

The material used consisted of Natural Rubber SIR 20, NaHCO₃ (UNIVAR), carbon black (CB) N330 (STD 3778-2003), Kaolin (325 mesh) bought from Belitung, Titanium dioxide (TiO₂) (A-120), Zinc oxide (ZnO) (NC-105), Stearic Acid (CH₃(CH₂)₁₆COOH) (SA-1806), CaCO₃ (28365000), Tetramethyl thiuram disulphide (TMTD) (HG/T2334-2007), Benzothiazyl-2-cyclohexyl-sulphenamide (CBS) (WILLING), santoflex 6PPD (FLEXYS), Paraffinic E-245, and curative agent Sulphur 99.9% (MIDAS SP-325).

The equipment is rubber mixing two roll mill-S (X) K-160 A, analytical balance capacity 3200 grams METTLER TOLEDO ME3002, infrared thermometer brand KRISOW-KW08-280, and moulding.

2.2. Methods

Natural rubber and chemical ingredients weighted were based on the formula as shown in Table 1. Natural rubber from each treatment was masticated for 15 minutes using two roll mill, then, molded into a sponge using moulding at 140°C for 15 minutes.

Sponges were analysed for mechanical properties including specific gravity with ASTM D 624 test method, compression set, 25% defl, 70°C, 22h (ASTM D 395); tensile strength, ASTM D 412; tear strength (ASTM D624); and elongation at break (ASTM D412). SEM and TGA were tested to observe the surface area morphological and its thermal properties of the sponges.

Table 1. Formulation of Sponges using Kaolin and CaCO₃ Filler.

Materials	Formula (phr)		
	A*	B*	C*
NR		100	
TiO ₂		3.5	
CB		2.75	
ZnO		4.85	
CH ₃ (CH ₂) ₁₆ COOH		2.75	
NaHCO ₃		12.85	
Kaolin	6	8	10
CaCO ₃	40	38	36
6PPD		1.25	
TMTD		1.65	
CBS		0.85	
Parafinic Oil		5	
Sulphur		1.85	

3. Results and Discussion

Table 2. Physical Mechanical and Tensile Properties of Sponges based on Kaolin and CaCO₃.

Parameter	Formula		
	A	B	C
Specific Gravity	0.48	0.51	0.54
Compression Set (%)	22.64	28.05	29.63
Tensile Strength (N/m ²)	32.18	34.46	35.01
Elongation at Break (%)	220	212	197

Table 2 shows the specific gravity, compression set, tensile strength, and elongation at break of the sponges using Kaolin and CaCO₃ using NaHCO₃ as foaming agent. Meanwhile, the size of cavity formed was also depicted in Fig. 1(a-c). The added ingredients inhibited the performance of NaHCO₃ releasing CO₂ gas as a form of air cavity. According to Najib *et al.* [10] the amount of air cavity formed by NaHCO₃ influences the relative density value. In addition, the specific density affects the air cavity and the morphological surface of the sponges. As a result, the increasing of filler added in the sponge, the higher specific of the sponges.

A compression set test aims to see the ability of the sponge to withstand the load and return to its original state when the load is removed. The sponge set compression is related to the cavity, elasticity and strength of the structure of the constituent material. The compression set as listed in Table 2 shows that there is an increase in the value of form A to formula C. The difference in the compression set value of each treatment affected the structure and elasticity of the sponge produced. Structural strength and elasticity are related to the cross link bond density resulting from the vulcanization process. Cross link bonding and structural strength that form sponge porosity whose forming molecules are filled with CB,

kaolin, and CaCO_3 determine the ability of the sponge to withstand the load and return to its original state. According to Kinasih *et al.* [22] the addition of fillers can increase the cross linking formed. The cross linking formed by the fillers addition causes a slight difference in the compression set values for each formula as listed in Table 1. In addition, the filling material is added to the optimum ratio to maintain the elastic properties of rubber at a certain pressures and times [9].

Tensile strength testing aims to determine the maximum sponge tension to hold the strain when pulled before breaking. As shown in Table 2, 51 phr addition for the formula yields the tensile strength of 35.01 N/m^2 . It could be said that the number of filler (CaCO_3 and kaolin) has an impact on the tensile strength. While, elongation at break also influenced by the number of filler, softening agent, and the amount of air cavity. In addition, the NR that used in the sponges also contribute to the elasticity since NR has an excellent tensile property.

3.1. Morphological Properties

Fig. 1 shows the sponge morphology of micrographs SEM to determine the size and distribution of cavities formed. Tests for all samples (A; B; and C) were carried out by means of magnification (250; 500; and 1000) times. The results of measurements of cavity/porosity and distribution of materials in vulcanization as shown in Fig. 1.

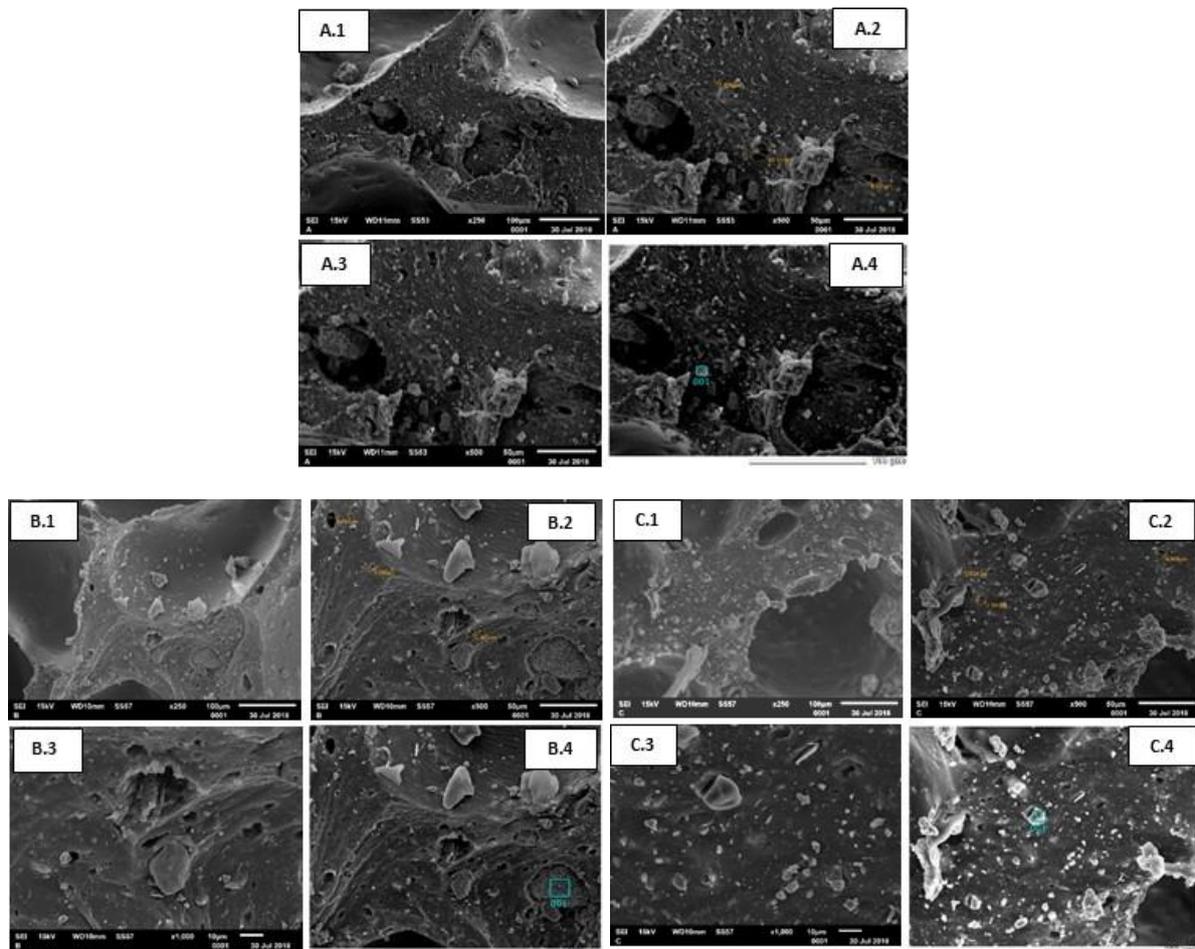


Figure 1. Micrograph of SEM for formula A, B, and C with the magnification 250x (1); 500x (2); 1000x (3).

The measurement results of porosity with SEM for samples from the treatment (A; B; and C) resulted in varying air cavity diameters. Air volume that varies in volume occurred because CO₂ gas being trapped between compound-forming molecules when heated in a mould. According to Kim and Kim [23] air cavities occur due to the trapped air when the composite was heated. The non-uniformity of air cavity formed was likely to occur from the distribution of fillers and chemical ingredients not evenly distributed. Another possibility was caused by the propagation of heat throughout the compound during uneven vulcanization processes which results in varying amounts of CO₂ gas produced. Cavity/porosity for samples (A; B; and C) was 3.225 μm; 13,242 μm and 6,835 μm. Measurement results of sample B cavity/porosity formed 3,688 μm; 5,367 μm and 8,881 μm. The measurement results of sample C found various cavity sizes/porosity 2.628 μm; 7,155 μm and 6,986 μm. The diversity of the size of the porosity formed is influenced by the ratio of filling material, geometric shape of the material, the surface properties of the material and the size of the material grain.

Furthermore, SEM micrographs test results for the three samples (A; B; and C) found several elements in the form of Au, Ti, Ca, Si, Al, Na O and C. Elements with a major content found were Ti, Au and elements with minor content of Ca and Si, Al, Na, O and C. The effect of ZnO, CH₃(CH₂)₁₆COOH, and TMTD causes faster cross-linking between rubber and sulphur [24]. The addition of activator, co-activator, accelerator and sulphur as vulcanizing material causes cross-linking between strongly thick molecules with a homogeneous level of maturity.

3.2. Thermal Gravimetric Analysis

Fig. 2 how the results of TGA in order to measure changes in weight/mass reduction as a function of temperature and time as well as predict the thermal stability that occurs. Nitrogen gas used in the sample was conditioned at a flow rate of 75 mL/min by heating at temperatures of 50°C to 560°C at rate 10°C/minute. Next, it cooled to 300°C until it reached a balance in 2 minutes. Furthermore, nitrogen gas as a cleaner was conditioned at a flow rate of 75 mL/min with combustion heat of 300°C to 800°C at rate 10°C/minute. Measurement results of sample A; B; and C shows that a decrease in sponge mass weight is directly proportional to the decrease in weight of the constituent material as listed in Table 1.

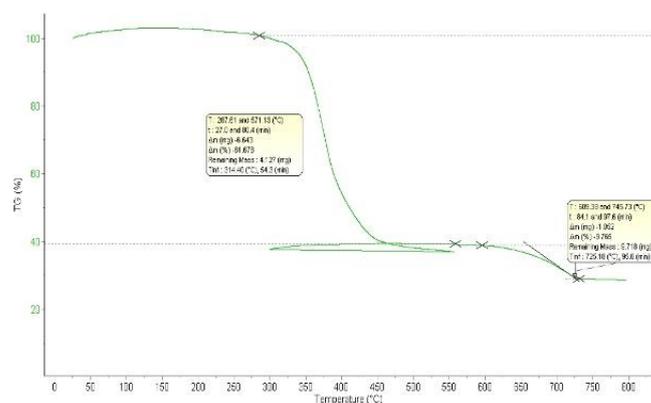


Figure 2. Thermogram of Sponge using Formula A using Kaolin: CaCO₃ (6:40) phr.

The results of formula A measurement for sponges from RCKC and other process materials show that there is a loss of mass relative to the polymer by increasing the combustion temperature as depicted in Fig. 2. Significant loss of polymer mass weight in the first phase at temperatures 287.61 to 571.13°C from 27.0 to 80.4 minutes there was a mass loss of 61.678% consisting of natural rubber, carbon black, NaHCO₃, kaolin, CaCO₃, and TiO₂. For paraffinic oil, TMTD, 6PPD, CBS, and sulphur are very small. Calcium carbonate during combustion with oxygen decomposes into CaO and CO₂. The thermal decomposition process will accelerate along with the combustion time, where at the same time there is

a wide reduction in the surface of the particle (Mohamed et al., 2012). Then at temperatures 609.38 to 745.73oC during combustion time of 84.1 to 97.6 (minutes) a mass loss of 9.675%.

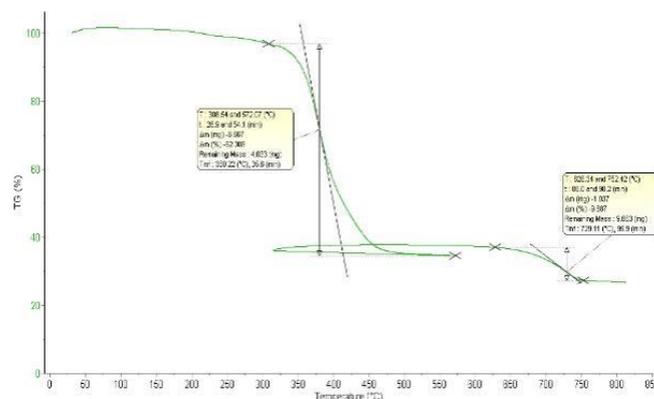


Figure 3. Thermogram of Sponge using Formula B using Kaolin: CaCO_3 (8:38) phr.

Fig. 3 shows the thermogram of formula B, it could be seen that there is a decrease in mass weight relative to the first phase of the time 28.9 to 54.1 minutes at temperatures 308.54 to 572.07°C. The mass lost from the sponge is 62,308% with a remaining mass of 4,003 mg. Mass loss (9,687%) occurred in the second phase at 8.60 minutes until 98.2 minutes. Mass loss in the 2nd phase occurs at temperatures of 628.34 to a temperature of 752.42 minutes. The remaining mass in combustion is 729.11°C for 95.9 minutes in the second phase of 9,663 mg.

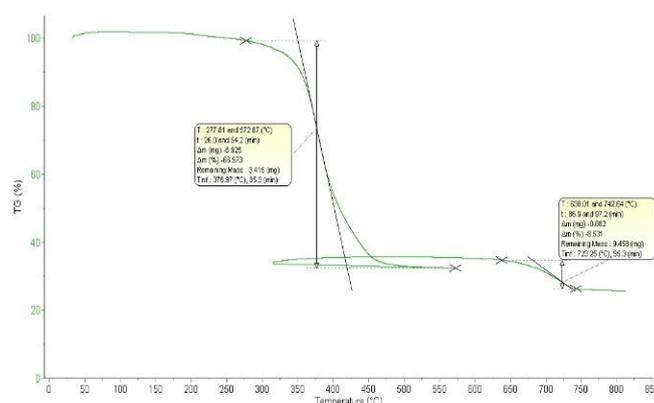


Figure 4. Thermogram of Sponge using Formula C using Kaolin: CaCO_3 (10:36) phr.

The sponge measurement results from sample C show that based on the thermogram in Fig. 4 shows, there was a decrease in mass weight relative to the first phase of the time of 26.0 to 54.2 minutes at temperatures 277.81 to 572.87°C. The weight of sponge mass lost from RCKC and other chemical materials is 66,973% with a mass remaining 4,415 mg. Mass loss in the second phase occurred at 86.9 minutes to 97.2 minutes at combustion temperatures of 638.01 to 742.64°C as much as 8,531%. The remaining mass that does not burn in the second phase is 723.25°C for 95.3 minutes as much as 9,458 mg.

4. Conclusions

Modification of natural rubber, carbon black, kaolin, Calcium Carbonate fillers with NaHCO_3 as blowing agents of the three treatments produced sponge with different mechanical properties. Test results for samples from Formula B with specific gravity 0.51, compression set 28.05%, tensile strength 34.46 N/m², and elongation at break 212%. SEM testing of sample B cavity formed 3,688 μm ; 5,367 μm and 8,881 μm . The SEM test results for the three samples (A; B; and C) in positions (1; 2; and 3) were found in elements Au, Ti, Ca, Si, Al, Na O and C. The elements with the major content found were Ti, Au and elements with minor content of Ca and Si, Al, Na, O and C. The results of thermal gravimetric analysis for all samples occur relative mass loss.

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