

# Thermal, Morphological and Physic-Mechanical Properties of Natural Rubber - CaCO<sub>3</sub> Composites Using Jatropha Oil as Softener.

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**Abstract** The urgency of green technology in rubber compounding has become a critical issue recently. In this research, the effect of using renewable resources in rubber compounding has been studied. Commercial Calcium Carbonate, Silica and Jatropha Oil were used in natural rubber composite. The research was designed by varying the types of commercial filler namely CaCO<sub>3</sub> (47-51) phr, silica (47-51) phr and Jatropha Oil (4-6) phr in natural rubber composites (SIR-20). The formulas were intentionally designed for rubber tips vulcanizates. The samples were characterized by the determination of physic-mechanical, thermal (TGA) and morphological (SEM) properties. From the measured results, there is no significant effect on the tensile strength, specific gravity, and hardness on the loading of commercial CaCO<sub>3</sub> and Silica in natural rubber composites using Jatropha Oil. However, a slight difference in elongation at break and abrasion resistance could be detected. Compared to the commercial rubber tips, the rubber tips produced in this research have higher tensile strength, elongation at break and abrasion resistance. Due to the usage of commercial CaCO<sub>3</sub> and Silica, the SEM micrographs show rough surface because of the agglomeration. The thermogram shows clearly the compositional analysis of the rubber tips vulcanizates consist of Jatropha Oil and natural rubber, CaCO<sub>3</sub>, ash and other filler residues such as Silica.

## 1 Introduction

Fillers play an important role in rubber composites to enhance physic-mechanical properties and reduce the material costs since the second highest portion of the manufacturing of rubber products [1, 2]. Fillers are grouped into two types reinforcing and non-reinforcing fillers. Fang, Song [3], [4] mentioned that the reinforcing such as Carbon Black (CB), SiO<sub>2</sub> has been used to improve the modulus and strength of rubber products, whereas, non-reinforcing have not significant effect on the rubber properties.

CB consumption of world rubber industry has been increasing recently. Meanwhile, the increasing of rubber industries development is in the same way with the increasing price of CB per year [5]. On the other hand, CB is obtained from derivative oil industries [6], while the petroleum reserves in the world are getting less [5]. Therefore, it is a need to find CB substituents that are renewable, low cost, abundant and environmentally friendly. Considering its availability from natural resources, Calcium Carbonates (CaCO<sub>3</sub>) is an prospective filler to be developed for rubber and plastics industry.

CaCO<sub>3</sub> is a low-cost commercially available and is able to be non-reinforcing filler that only upsizing the volume of the rubber products [7, 8]. Furthermore, CaCO<sub>3</sub> is also able to impart significant improvements on polymer properties, such as abrasion resistance, stiffness and tensile strength as well as thermal stability [9] and Fang, Song [3], [8, 9] reported that to improve the mechanical properties of the reinforced natural rubber-CaCO<sub>3</sub> composites. According to Avella, Errico [10], the benefits of blending polymer with the CaCO<sub>3</sub> reduce cost

without losing the tensile properties significantly. [9], Bartczak, Argon [11] stated that the selection of appropriate size distribution and surface treatments with hydrophobic agents such as stearic acid and silane.

Fang, Song [3] observed that rubber composite filled chain shape Nano Calcium Carbonates (NCC) has positive benefits on Mullin effects, Payne effects, and its dynamic characteristics. While Lazzeri, Thio [12], [13] showed that the surface modified Calcium Carbonates also exhibited better processing capability than that Carbon Black in SBR vulcanizates. In addition, the improvement on mechanical properties, however, is always limited because Calcium Carbonates with high surface energy tends to agglomerate [8, 9]. Qu, Chen [14] found that when the amount of co-precipitated Nano Calcium Carbonates and bulk NCC is identical, the mechanical properties of the former can achieve high tensile strength (13,38 MPa) which was superior over the later.

In rubber industry, Calcium Carbonates is also commonly used as the filler for SBR composites [13, 14], Acrylonitrile-butadiene rubber [15], and Chloroprene composites [16, 17]. Fang, Song [3], [9, 14] stated that addition NCC can produce outstanding stiffness, toughness, and dimensional stability rubber compound. Hence, the deep understanding of the relationship between particle size and mechanical properties are important to improve the end-user properties of rubber composite.

Focusing on the industrial application (end-use rubber composite), this research applied commercial precipitated CaCO<sub>3</sub>, which is finer and

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high purity (400 mesh) along with the commercial Silica for natural rubber composite.

Bearing in mind the green technology approach, the importance of searching new alternative is not only for CB as filler but also mineral plasticizers [18-21]. With regard to some weakness of using mineral plasticizers such as high cost, low availability, corrosive and toxic chemicals [21, 22], in this research would apply commercially natural plasticizer namely Jatropha Oil (Ricini Oil). Gogoi, Boruah [23] has conducted research on the use of jatropha seed oil and other vegetable oils as coupling agents as well as plasticizers in the range of 1-3 phr. The other research showed that it had a significant effect on mechanical properties such as modulus, tear strength, and hardness [22-24]. Based on the previous researchers, Jatropha seed potentially could be used as plasticizers to substitute the mineral oil.



Figure 1. Rubber tips products

Thus, the current study focuses on the incorporation of commercial fillers such as Silica and Calcium Carbonate into natural rubber composites using natural based plasticizers. The tensile properties, physic-mechanical properties, thermal and morphological properties were investigated. The usage of the NR composites was intentionally designed as manufacturing of rubber tips vulcanizates (end-up products) as shown in Figure 1. The product of this research was commonly used for furniture accessories, canes including quad canes and tripods. In order to observe the product specification compliance with this research, the commercial rubber tip was also examined. Consequently, the research would contribute new information about the essential properties rubber tips vulcanizates that using commercial CaCO<sub>3</sub>, Silica, Jatropha Oil in natural rubber composites. Thus, this technology could be applied for rubber tips manufacturing and rubber industries.

## 2 Experimental

### 2.1. Materials

Natural Rubber/ NR (Standard Indonesian Rubber/SIR 20) was used as polymer. The other compounding ingredients including Zinc Oxide (NC 105 Global Chemical Co, Ltd), Stearic Acid (SA 1806, Oleochemicals Industry, PT Sumi Asih), Carbon Black (CB N330, Vulcan, CABOT), Calcium Carbonate (400 mesh, SK Product), Precipitated Silica powder (Type SD Grade 185, Chemisil, PT

Supersilica Indo Semesta), TiO<sub>2</sub>, Sulphur. While, Jatropha Oil (Oleum Ricini), PEG-4000, TMTD, Paraffinic Wax, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine 6 PPD were obtained from Brataco Chemical.

### 2.2 Methods

#### 2.2.1. Rubber Compounding

The rubber compounding was carried out using a laboratory two roll mill XK-160, Shanghai Rubber- Machine Worker, China. NR was masticated in two roll mills for 2-3 minutes. The next process is adding the compounding ingredients as listed in Table 1, so that the 5 vulcanized sheets were obtained. This process was conducted based on ASTM D3182 Standard Practice for Rubber (Materials, Equipment, and Procedures) for Mixing Standard Compounds and Preparing Standard Vulcanized Sheets. The vulcanized sheets were pressed for 12 minutes at 125 °C. The formulas given in Table 1 were developed for rubber tips products (end –up). Therefore, in this research, the rubber tips in market (F6) would be tested to compare its quality. In order to obtain the accurate data, the rubber compounding and rubber tips pressing were conducted as 3 replications for each formulas.

Table 1. Formulation of Rubber Compounding for Rubber Tips

Material	Formula				
	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>
NR (SIR 20)			100		
TiO <sub>2</sub>			3.65		
Carbon Black			0.85		
ZnO			4.65		
Stearic Acid			2.44		
Silica	47	48	49	50	51
Calcium Carbonate	51	50	49	48	47
Jatropha Oil	4.5	5.00	5.50	6.00	6.50
PEG			3.85		
TMTD			1.58		
Paraffin Wax			0.82		
6.PPD			1.25		
Sulfur			2.75		

Note : F6 is the commercial rubber tips

#### 2.2.3. Physical-Mechanic Properties Testing

The five formulas for solid tyres were tested for parameters as follows hardness Shore A (ASTM D 2240-05 (ra 2010); tensile strength (ASTM D 412); modulus 300% (ASTM D 412); specific gravity (ASTM D 297-93 (ra 2002); abrasion resistance (ASTM D 5963-04 (ra 2010). Each replication was tested for those parameters, the data presented in this results are the average of 3 replications.

### 2.2.4. Scanning Electron Microscope and Thermal Gravimetry Analysis

Thermal Gravimetric Analysis was conducted using LINSEIS STA PT 1600 based on Standard Test Method for Rubber – Composition Analysis by Thermogravimetry – ASTM D 6370-99 (2003). Heat from 30-800 °C, 10 °C/min. While, the morphological analysis of NR-Calcium Carbonates composites was examined using SEM JEOL JSM 6510.

## 3 Results and Discussion

### 3.1 Tensile Properties

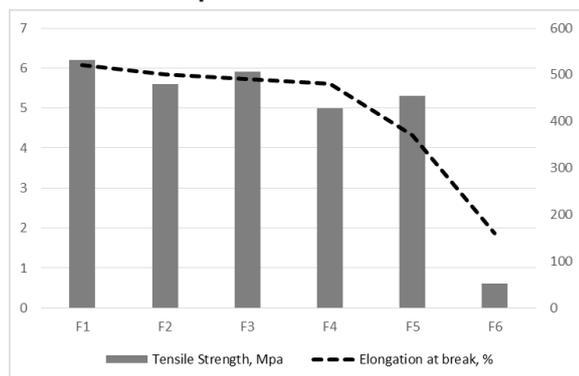


Figure 2. Tensile Properties of NR-CaCO<sub>3</sub> Composites Using Jatropa Oil

The relationship between tensile strength and loading of precipitated CaCO<sub>3</sub> and Silica in NR vulcanizate is presented in Figure 2. It could be seen that the tensile strength of F1 (47 phr Silica and 51 phr CaCO<sub>3</sub> loading) has the highest number about 6,2 MPa. The graph illustrates the fillers loading (F1, F2, F3, F4, and F5) may not influence the tensile strength of NR vulcanizate significantly. The tensile properties is influenced by the interaction between the fillers and rubber within the vulcanizate along with the cross linking density [4, 25]. Even though the rheological properties were not examined in this study, the using CaCO<sub>3</sub> as non-reinforcement filler in a high proportion would affect on cross-linking interaction between fillers and rubber matrix negatively [7, 13, 14]. The using of 400 mesh CaCO<sub>3</sub> and commercial Silica as fillers which were very large particle size probably could not produce more interfacial bonding and causes the molecular mobility to increase resulting in the stiffening of the matrix. Furthermore, the precipitated CaCO<sub>3</sub> in very large number possesses a low surface area and initiate to form agglomerate in the rubber filler interaction [14, 25]. Therefore, when it incorporates into natural rubber composites cause severe reduction of the elongation at break [7, 10, 11]. The decreasing of elongation at break is shown in Figure 2. It indicates that the more loading CaCO<sub>3</sub> (non-reinforcement filler) causes the worse interaction between filler and natural rubber matrix in the composites.

However, compared to the tensile strength of F6 (commercial rubber tips), the NR vulcanisates in this formula has higher tensile properties (tensile strength and elongation at break). The nature of NR has very high tensile properties among other polymers [26].

### 3.2. Physical and Mechanical Properties

Table 2. Physical and Mechanical Properties of NR-CaCO<sub>3</sub> Composites Using Jatropa Oil

Formula	Specific Gravity, g/cm <sup>3</sup>	Hardness, Shore A	Abrasion Resistance, DIN, mm <sup>3</sup>
F1	1.392	55	233.8
F2	1.338	50	226.8
F3	1.540	56	324.8
F4	1.395	55	204.8
F5	1.391	56	195.4
F6*	1.598	73	778.8

\* ) commercial rubber tips

Table 2 lists the physic-mechanical properties of rubber tips vulcanized namely specific gravity, hardness and abrasion resistance. The changing hardness with different loadings of CaCO<sub>3</sub> and Silica in NR vulcanizate is shown in Table 2. It was observed that the fillers used in this composites have no significant influence on hardness of the vulcanizate. As listed in Table 1 that the quantity of reinforcement filler (Silica) and Calcium Carbonates as non-reinforcement filler is not significantly different. This very slight variation could not give significant changing on hardness and specific gravity as well. Aforementioned in tensile properties, the particle size, shape and surface area of fillers has a significant role on the hardness of vulcanizate [11, 14, 18, 25]. Therefore, using very fine reinforcement filler in natural rubber composites such as Carbon Black (CB) is suggested to increasing the rigidity and stiffness of the vulcanizates [12, 25]. The higher hardness due to the very good dispersion between filler and rubber in polymer matrix that causes increasing the cross linking density of rubber composites [7]. In this research, the fillers CaCO<sub>3</sub> and silica do not have the other advantages of CB like the functional groups of CB could form sulfuric cross-linking and also Van Der Walls interaction in the rubber matrix.

Compared to the commercial rubber tips, the 5 formulas have smaller specific gravity and lower hardness. The hardness of rubber tips commercial is about 73 Shore A, while the 5 formulas (F1, F2, F3, F4, and F5) only approximately 55 Shore A. The quantity of reinforcement filler should be added in a certain amount to improve its physical properties.

The physic-mechanical properties namely abrasion resistance was examined and evaluated. Table 2 illustrates the value of abrasion resistance

each formula and the commercial rubber tips. The test method (ASTM D 5963-04) is subject to abrasive/ frictional wear in actual service. This test was conducted to evaluate the product specification compliance. By comparing test results of the designed formula (listed in Table 1) in this research to the commercial rubber tips in the market, some recommendations could be reported. The interpretation of the testing is expressed as volume loss in cubic millimeter, a smaller number indicates better abrasion resistance. As listed in Table 2, the abrasion resistance of commercial rubber tips 778,8 mm<sup>3</sup>. In contrast for other formulas (F1, F2, F3, F4 and F5) have considerably small volume loss (200-300 mm<sup>3</sup>), which indicates has a better abrasion resistance.

### 3.3 Morphological Properties

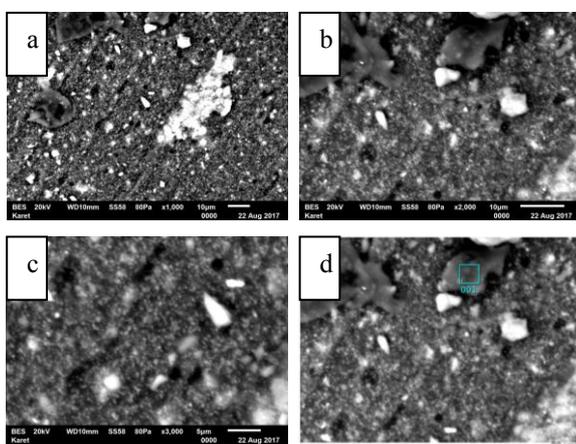


Figure 3. SEM Micrographs for Vulcanized of Natural Rubber- CaCO<sub>3</sub> Composites (100:47) using Jatropa Oil a) 1000x, b) 2000x, c) 3000x magnification. d) analysis on 20 um

The SEM micrographs for Vulcanized Rubber of NR-CaCO<sub>3</sub> 100:47 phr is shown in Figure 3. The magnification of the composites figure were 1000X, 2000X, 3000X a, b, c respectively while the micrographs were magnified for quantitative analysis.

It could be seen clearly that the micrographs show an irregular surface which is not so smooth and very rough. It indicates that the dispersion between CaCO<sub>3</sub> in the NR rubber matrix using Jatropa Oils is not homogenous so that the surfaces are not smooth (irregular surface). Since the particle size of CaCO<sub>3</sub> (400 mesh) is not Nano-sized, the agglomeration could not be hindered, and the flocculation appear on the surface, so that the sample has thicker tear lines and rough surface. Fang, Song [3] stated that using Nano-calcium carbonates (NCC) with spherical and cube shape has a positive effect to the Mullins effects and the filler networking in the rubber matrix. Therefore the micrographs show clear and smooth surfaces. Consequently, using the

smaller NCC has the outstanding mechanical and tensile properties that resulted from good dispersion in the NR composites as observed in SEM micrographs [3, 8, 9, 18]. Conversely, the large size of CaCO<sub>3</sub> using in this research, the non-homogenous dispersion of CaCO<sub>3</sub> and Jatropa Oil in the rubber matrix contributed to the flocculation which had negative effects on the mechanical properties as shown in table 2.

The micrographs indicate that the rubber blends undergo ductile failure. So that, the failure of the tensile test (as shown in table 1) could be explained by the phenomena. Compared to the composite using Carbon Black which has finer particle size rather than CaCO<sub>3</sub>, the surface has the smoother surface and better tensile properties [8, 18, 27]

### 3.4 Thermal Properties

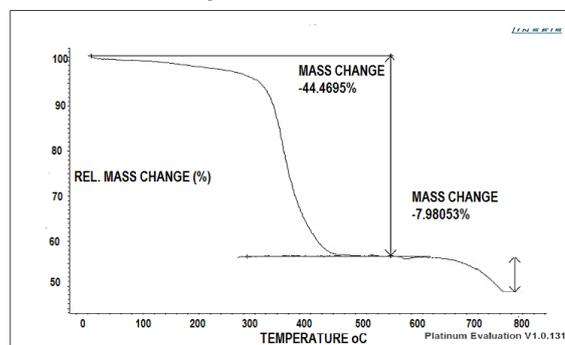


Figure 4. Thermogram for Vulcanized of Natural Rubber- CaCO<sub>3</sub> Composites (100:47) using Jatropa Oil.

The thermogram as shown in Figure 4 shows the curve of relative mass loss of the polymer by the increasing of temperature. The polymer as shown in table 1 consists of the major quantity of NR, filler SiO<sub>2</sub>, and CaCO<sub>3</sub> 100, 51, and 47 phr respectively and very small quantity of Jatropa oil 6.5 phr. TGA was examined to observe the weight changing to changes in temperature (thermal stability), components in the polymer, organic and inorganics existed in the polymer, and residues percentage [28]. In order to obtain accurate weight loss, the derivative curve was used with the high-resolution dynamic method. Firstly, Nitrogen gas was purged with the flow 75 ml/min for sample, heating until 50 °C and allow to equilibrate for 2 minutes. Secondly, heat from 50 °C to 560 °C at 10 °C/min. Then, cool at about 300 °C and allow to equilibrate for 2 minutes. The purge gas changed to air at 75 ml/min, and heat from 300 °C to 800 °C at 10 °C/min. This changes due to the composites contain CaCO<sub>3</sub> as filler which decomposed at 680 °C - 800 °C, thus oxygen was applied in order to see the decomposition clearly [29, 30]. In the presence of Oxygen, the CaCO<sub>3</sub> was decomposed into CaO and CO<sub>2</sub> [29]. As shown in Figure 4, at the 300 °C, the decreasing weight is about 5%, probably, this is the loss of Jatropa oil and other oils ingredients in the sample. At the 550 °C, the natural rubber and all organic materials were

burn, which is about 45 % of composites weight. While, the 7.9% mass change in the range 600 °C – 800°C is the decomposition of CaCO<sub>3</sub>. The residual which about 48% weight loss at the temperature above 800°C indicated the ash and filler residue. As listed in Table 1, the number of SiO<sub>2</sub> and TiO<sub>2</sub> is 51 and 3.65 phr respectively, so that relative mass change at 800°C is considerably high. Similarly, the thermogram typical and its compositional analysis (Figure 4) which using CaCO<sub>3</sub> as filler was also obtained for SBR vulcanizate [31], for NR and SBR blending [29]. Furthermore, to obtain the more accurate decomposition and compositional analysis, the ending temperature should be about 1300 °C.

## Conclusion

In conclusion, there is no significant improvement in the tensile strength, specific gravity, and hardness on the loading of commercial CaCO<sub>3</sub>, Silica in natural rubber composite using commercial Jatroppha Oil. However, a very slight difference in elongation at break and abrasion resistance could be detected due to the increasing loading of CaCO<sub>3</sub>. The rough surface appears in SEM micrograph indicates the non-homogenous dispersion between commercial CaCO<sub>3</sub>, silica in natural rubber composites. Consequently, the vulcanisates have a slightly lower physic mechanical properties rather than commercially rubber tips. Based on the thermogram analysis, about 44% weight of the jatroppha oil and other organics components completely loss at 500 °C, while 8% weight of the CaCO<sub>3</sub> was decomposed into CaO and CO<sub>2</sub> at 680 °C – 800 °C. In addition, the residual (48% weight) is expected an organic materials, ash and filler residues (Silica and TiO<sub>2</sub>).

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