*Maejo Int. J. Sci. Technol.* **2012**, *6*(02), 249-258

Maejo International
Journal of Science and Technology

**ISSN 1905-7873**

Available online at www.mijst.mju.ac.th

*Full Paper*

# Comparative properties of natural rubber vulcanisates filled with defatted rice bran, clay and calcium carbonate

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*Received: 8 April 2011 / Accepted: 12 July 2012 / Published: 13 July 2012*

**Abstract:** The effects of defatted rice bran (DRB) as a filler for natural rubber vulcanisate on its cure characteristics, mechanical properties and morphology were investigated. The properties of the DRB-filled vulcanisate were also compared with clay-filled and $CaCO_3$-filled vulcanisates. At similar loading level (50 parts per hundred of rubber), DRB-filled vulcanisate gave the shortest cure time. Clay-filled vulcanisate showed highest tensile and tear strength followed by DRB-filled vulcanisate. However, $CaCO_3$-filled vulcanisate gave highest rebound resilience while DRB-filled vulcanisate exhibited highest modulus, hardness and abrasion resistance. Scanning electron micrographs revealed that the morphology of clay-filled vulcanisate was more homogenous than that of DRB-filled and $CaCO_3$-filled vulcanisates. According to these observations, DRB can potentially be used as a cheap and more environment-friendly natural filler when an improvement in mechanical properties was not so critical.

**Keywords:** natural rubber, vulcanisate, rubber filler, defatted rice bran

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## INTRODUCTION

Fillers are compounding ingredients added to rubber compounds for the purpose of reinforcing them and/or cheapening their cost. Traditional fillers include carbon black, silica, calcium carbonate, calcium silicate and clay. Carbon black is the most popular filler added to the rubber compounds due to its ability to enhance certain properties, especially mechanical properties [1-3]. Clay and calcium carbonate are considered as useful fillers in rubber compounds because of their low cost. Much work [4-7] has been done to study the use of clay and calcium carbonate as fillers for rubber compounds. Apart from the traditional fillers, the use of renewable materials such as starch, rice husk, rice husk ash, wood sawdust, rubber wood and soy meal have also appeared in the literature [8-18]. Fillers derived from renewable materials have attracted interest because of their low cost, renewability and environment-friendly nature.

Rice bran is a by-product of the rice-milling process. It is also the source of high-quality edible oil (rice bran oil). Rice bran oil is extracted from rice bran, leaving defatted rice bran (DRB) as by-product. DRB is used to reduce the final cost of animal feed or is discarded as agricultural waste. However, it still contains significant amounts of protein, carbohydrate, dietary fibre and phenolic substances [19]. To upgrade the value of DRB, we explore its possible application as a filler in rubber compounds. The effects of DRB on the morphology, cure characteristics and mechanical properties of vulcanised natural rubber (NR) are investigated in this paper. The properties of the DRB-filled vulcanisate are also compared with clay-filled and $CaCO_3$-filled vulcanisates.

## MATERIALS AND METHODS

### Materials

All materials were used as received. NR (STR 5L), elemental sulphur ($S_8$), stearic acid, zinc oxide, accelerators and antioxidant (polymer of p-cresol; Lowinox® CPL) were purchased from Lucky Four Co. Ltd. (Thailand). Two types of accelerators used were dibenzothiozyl disulphide (Vulkacit® MBTS) and tetramethylthiuram disulphide (Vulkacit® TMTD) (97% purity). Stearic acid and zinc oxide were of rubber-grade. Three fillers used were DRB, china clay (hydrated aluminium silicate) and ground calcium carbonate ($CaCO_3$). Clay and calcium carbonate were purchased from Lucky Four Co. Ltd. and DRB (composition shown in Table 1) was purchased from Thai Edible Oil Co. Ltd.

**Table 1.** Composition of DRB

| Component | % |
|---|---|
| Crude protein[1] | 17.57 |
| Crude fibre[1] | 9.19 |
| Moisture content[1] | 11.10 |
| Crude fat and oil[1] | 1.40 |
| Carbohydrate[1] | 49.74 |
| Ash[2] | 11.00 |

[1] Laboratory of Animal Nutrition Research and Development Centre, Kasetsart University
[2] Laboratory of Dairy Research and Development Centre, Kasetsart University

DRB was passed through a 150-mesh screen and dried in a circulating air oven at 70°C for 17 hr before mixing. The Brunauer-Emmett-Teller (BET) surface area and porosity of the fillers were determined with a nitrogen adsorption instrument (Quantachrome Autosorb-1, Quantachrome Corp., USA) according to ISO 9277 [20]. The samples were degassed at 100°C for 24 hr in the degas pot of the adsorption instrument in order to remove moisture and other contaminants before measurements, which were done at the boiling point of nitrogen (-196°C). The amount of adsorbed gas was measured to determine the surface area and porosity of the surface. The calculation was based on the BET theory [20]. The results are given in Table 2.

**Table 2.** Physical properties of different types of fillers

| Filler | Specific surface area ($m^2/g$) | Pore volume (cc/g) | Pore diameter (Å) |
|---|---|---|---|
| DRB | 4.63 | 0.0074 | 64.09 |
| Clay | 5.83 | 0.0182 | 124.80 |
| $CaCO_3$ | 4.46 | 0.0136 | 122.00 |

## Preparation of Rubber Compounds and Vulcanisates

All rubber compounds contained the same chemical composition except for the filler type. For each rubber compound, 50 parts per hundred of rubber (phr) of the filler content was used. The ingredients used in each compound are listed in Table 3. The four compound formulations are designated as control (no filler), DRB, clay and $CaCO_3$. The mixing was carried out both in an internal mixer (model YFD-3L, Yong Fong Machinery Co. Ltd., Thailand) and a two-roll mill (model YFTR-8, Yong Fong Machinery Co. Ltd., Thailand). All ingredients except sulphur were mixed with the rubber in the internal mixer with a fill factor of 0.7 at 80°C and a rotor speed of 50 rpm. The mixing sequence is shown in Table 4. After discharging, the compounds were further masticated in the two-roll mill for 2 min. Then sulphur was added and mixed with the rubber compounds for 3 min. Finally, the rubber compounds were taken out and sheeted through a two-roll mill. The rubber compounds were compression-moulded at 150°C using a hydraulic hot press (OOMN semi-automatic moulding press model HPC-100(D), Shanghai Zimmerli Weili Rubber and Plastic Machinery Co. Ltd., China) according to their respective cure time ($t_{90}$) from the cure curves.

**Table 3.** Formulations of rubber compounds

| Ingredient | Amount (phr) | | | |
|---|---|---|---|---|
| | Control | DRB | Clay | $CaCO_3$ |
| NR (STR 5L) | 100 | 100 | 100 | 100 |
| Sulphur | 2.5 | 2.5 | 2.5 | 2.5 |
| Stearic acid | 2 | 2 | 2 | 2 |
| Zinc oxide | 4 | 4 | 4 | 4 |
| MBTS | 1 | 1 | 1 | 1 |
| TMTD | 0.5 | 0.5 | 0.5 | 0.5 |
| CPL | 1 | 1 | 1 | 1 |
| DRB | - | 50 | - | - |
| Clay | - | - | 50 | - |
| $CaCO_3$ | - | - | - | 50 |

Note: phr = parts per hundred of rubber

**Table 4.** Mixing sequence of ingredients in the internal mixer

| Minute of addition | Operation |
|---|---|
| 0 | Loading of NR |
| 1 | Mastication of NR |
| 5 | Addition of stearic acid |
| 6 | Addition of zinc oxide |
| 7 | Addition of half of filler |
| 9 | Addition of MBTS, TMTD and CPL |
| 11 | Addition of rest of filler |
| 13 | Discharging |

Note: For control blend, total mixing time was 9 min. (no filler addition)

## Cure Characteristics

The cure characteristics of the different rubber compounds were evaluated using a moving die rheometer (model UR-2010, U-CAN Dynatex Inc., Taiwan) which was operated at 150°C with 3° arc for 60 min., following ISO 6502 [21]. Minimum torque (ML), maximum torque (MH), scorch time ($t_s$) and cure time ($t_{90}$) were determined. The cure time, the time at which the rheometer torque increases to 90% of the total torque change on the cure curve, was obtained from the moving-die rheometer. The cure characteristics were evaluated in triplicate and the average values were used in data analysis.

## Mechanical Properties

The tensile properties were determined using an Instron universal testing machine (model 5569, Instron Corp., USA) with a crosshead speed of 500 mm/min., and 1-kN load cell. The specimens were stamp-cut from a 2-mm-thick compression-moulded sheet. The dimension of the test specimens used was type I according to ISO 37 [22]. The specimens were symmetrically placed at the grips of the testing machine to achieve uniform tension distribution over the cross section. The tensile strength was determined from stress at rupture while the modulus at 100% strain was evaluated from the tensile stress at 100% elongation. The elongation at break was also determined.

The tear strength, a measure of the resistance of a material to tear force, was measured with a Lloyd instrument (model LS500-9674, Lloyd Instruments Ltd., UK) according to ISO 34-1 [23] using type-B die. Nicked-tab-end specimens were cut from a 2-mm-thick compression-moulded vulcanised sheet. The tear strength was tested at a crosshead speed of 500 mm/min. using a 1-kN load cell.

The sample hardness was determined using a Shore A durometer (model HPE-A, Bareiss, Germany) in accordance with ASTM D2240-05 [24] It was determined at three different positions on the specimens (about 6-mm thick) and the median value was indicated.

An abrasion test was carried out according to DIN 53516 [25] using an abrasion tester (model AB 6252, Bareiss, Germany). The abrasion resistance of a sample was expressed as volume loss when a cylindrically shaped specimen of 6-mm thickness is abraded for an abrasion distance of 40 m with emery paper (60 grit) at a constant force of 10 N.

Rebound resilience was determined according to DIN 53512 [26] using a rebound tester (model Rebound Check-Pendolo Shob, Gibitre Instruments S.r.l., Italy) and a cylindrically shaped specimen of 13-mm thickness. Rebound resilience was calculated as follows: Percentage resilience = $(1 - \cos\alpha) \times 100$ where $\alpha$ is the maximum rebound angle [26].

Each mechanical property test was repeated five times and an average value was used in the data analysis.

### Scanning Electron Microscopy (SEM)

The phase morphology of the NR vulcanisates filled with different types of filler was examined using a scanning electron microscope (model JSM-5410LV, JEOL Ltd., Japan). Samples were cryogenically fractured in liquid nitrogen and then coated with a thin gold layer to prevent electrostatic charge during examination.

## RESULTS AND DISCUSSION

### Cure Characteristics

The cure characteristics of all NR compounds are shown in Table 5. The DRB-filled compound, with the highest torque difference, was comparable to the $CaCO_3$-filled compound. In general, the torque difference is an indicator of cross-link density of the vulcanisates [4]. Thus, a high torque difference of the DRB-filled compound indicated its high cross-link density.

It can be observed that the addition of fillers decreased the cure time of the rubber compounds. At a similar loading level of 50 phr, the DRB-filled compound exhibited the shortest cure time while compounds with clay and $CaCO_3$ showed comparable $t_{90}$. The scorch time of the filled NR compounds showed a trend similar to the cure time.

**Table 5.** Cure characteristics of different NR compounds

| Compound Type | Torque difference, MH-ML (dN m) | Scorch time, $t_{s2}$ (min.) | Cure time, $t_{90}$ (min.) |
|---|---|---|---|
| Control | 12.59 | 3.30 | 8.08 |
| DRB-filled | 18.78 | 2.16 | 4.18 |
| Clay-filled | 16.25 | 3.23 | 6.35 |
| $CaCO_3$-filled | 18.36 | 3.03 | 6.31 |

### Mechanical Properties

*Tensile Properties*

The tensile properties of the different NR vulcanisates aer shown in Table 6. The tensile strength of all filled vulcanisates decreased because of the inability of the fillers to support stress transferred from the rubber matrix [14]. At a similar filler loading, clay gave the highest tensile strength, which corresponds to its highest surface area, as shown in Table 2, followed by DRB. Sae-

Oui et al. [27] reported that the surface area is the most important factor controlling the tensile strength.

The effect of fillers on the modulus, an indication of material stiffness, at 100% elongation is also shown in Table 6. The vulcanisate with DRB showed highest modulus and was comparable to that with clay, while clay gave elongation at break comparable to that of the control, with DRB giving a lower value.

**Table 6.** Tensile properties of NR vulcanisates

| Vulcanisate | Tensile properties | | |
|---|---|---|---|
| | 100% Modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) |
| Control | 0.97 ± 0.07 | 20.09 ± 1.29 | 559 ± 71 |
| DRB-filled | 1.85 ± 0.14 | 7.09 ± 0.13 | 500 ± 28 |
| Clay-filled | 1.80 ± 0.53 | 17.50 ± 0.53 | 594 ± 1 |
| $CaCO_3$-filled | 1.44 ± 0.15 | 4.39 ± 0.72 | 360 ± 29 |

*Tear Strength*

A negative effect on the tear strength (Figure 1) was observed when the NR vulcanisate was filled with different fillers. Similar to tensile strength, the addition of the fillers somewhat reduced the tear strength of the vulcanisate. The results indicate that the tear strength seemed to be affected by the surface area of the fillers (Table 2) and also probably by a low rubber-filler interaction. At similar filler loading, clay gave the highest tear strength, followed by DRB.

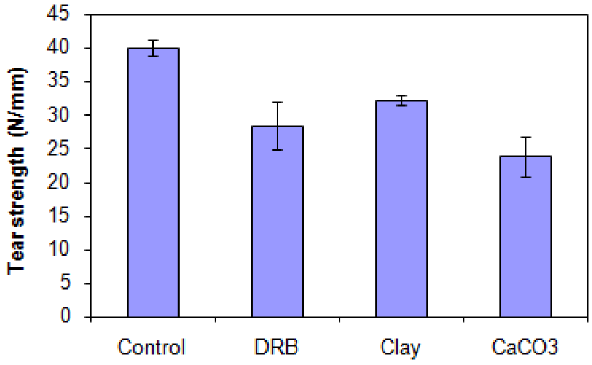


**Figure 1.** Tear strength of NR vulcanisates with different fillers (DRB, clay and $CaCO_3$)

*Hardness and Rebound Resilience*

The hardness values of the NR vulcanisates are shown in Figure 2. Compared to control, the filled vulcanisates exhibited higher hardness values, with DRB giving the highest value, followed by $CaCO_3$. The hardness values are seen to correspond to the torque difference values (Table 5), which indicates that the improvement in hardness of the filled vulcanisates was caused by an increase in the cross-link density of the vulcanisates. On the other hand, it can be seen (Figure 3) that the resilience of the vulcanisates, i.e. the elasticity of the rubber chain, slightly decreased with the addition of a filler.

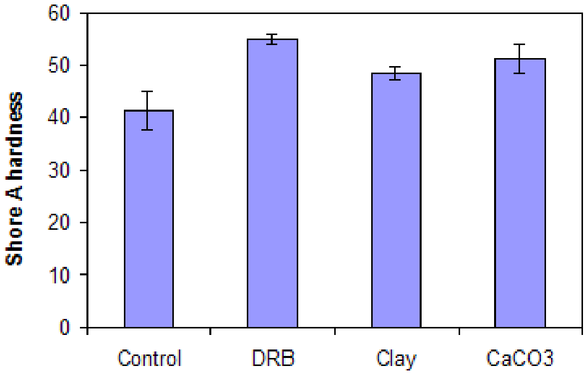


**Figure 2.** Hardness of NR vulcanisates with different fillers (DRB, clay and $CaCO_3$)

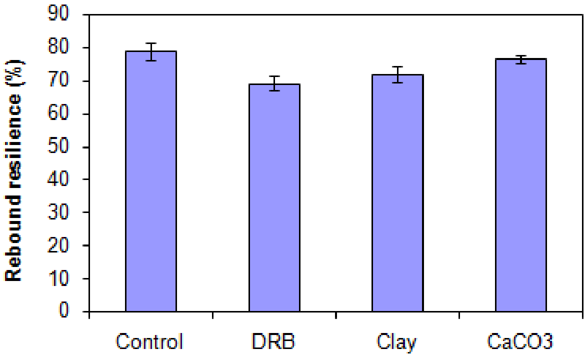


**Figure 3.** Rebound resilience of NR vulcanisates with different fillers (DRB, clay and $CaCO_3$)

*Abrasion*

The abrasion resistance of a solid body is defined as its ability to withstand the progressive removal of material from its surface as a result of the mechanical action of rubbing and scraping or of an erosive action [14]. The abrasion resistance of the NR vulcanisates, expressed as volume loss, is shown in Table 7; a higher volume loss means a lower abrasion resistance. The DRB-filled vulcanisate exhibited highest abrasion resistance and the control the lowest. The highest abrasion resistance of the DRB-filled vulcanisate corresponded to its highest hardness and cross-link density (Figure 2 and Table 5) while the control, with lowest hardness and cross-link density, also showed lowest abrasion resistance. Rattanasom and Chaikumpollert [28] also reported that the abrasion resistance of vulcanisates was contingent upon their hardness and cross-link density.

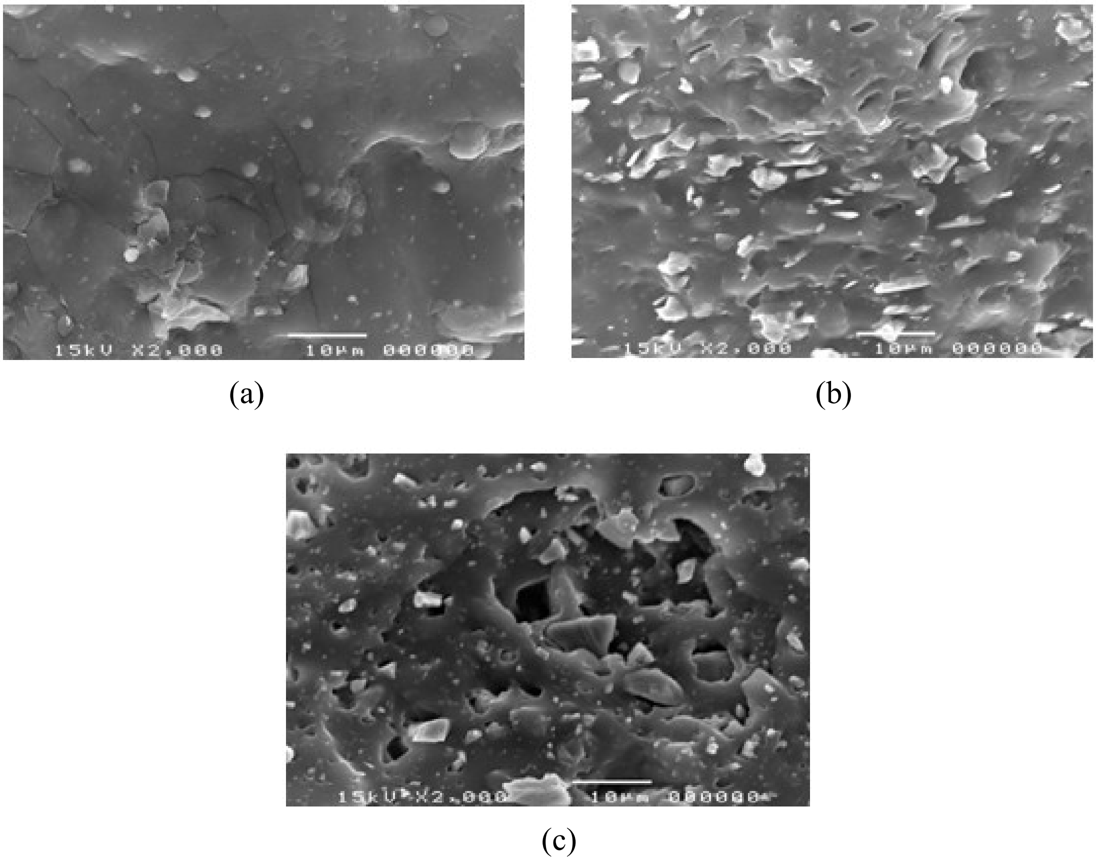
*Morphology Study*

Figure 4 shows scanning electron micrographs of the fractured surfaces of the NR vulcanisates blended with different types of fillers at 50-phr loading. Figure 4(a) shows an agglomeration of filler particles in the DRB-filled NR vulcanisate. This is expected because the

**Table 7.** Volume loss of NR vulcanisates

| Vulcanisate | Volume loss (mm$^3$) |
|---|---|
| Control | 66.27 ± 12.08 |
| DRB-filled | 38.05 ± 5.35 |
| Clay-filled | 51.08 ± 4.95 |
| $CaCO_3$-filled | 50.92 ± 5.07 |

interfacial interaction was weak due to the hydrophobic character of NR and the hydrophilic character of DRB. In the case of $CaCO_3$ filler, the filled NR vulcanisate showed several holes on the fractured surface on which the $CaCO_3$ particles were left (Figure 4(c)), which suggests that the interfacial interaction between the filler particles and the rubber was weak, resulting in the deterioration of the vulcanisate. Arayapranee and Rempel [14] also reported that the use of $CaCO_3$ as filler in NR/EPDM blends gave rise to many holes on the fractured surface due to a weak interfacial interaction. They found deterioration of the blend properties such as tensile and tear strength when compared with unfilled NR/EPDM blends. Figure 4(b) reveals that the clay particles were well dispersed without agglomeration within the rubber matrix. The dispersion of clay was better than that of the other fillers, thus contributing to a greater tensile and tear strength of the clay-filled vulcanisate.



(a) (b)

(c)

**Figure 4.** Scanning electron micrographs of fractured surfaces of NR vulcanisates filled with (a) DRB, (b) Clay and (c) $CaCO_3$

## CONCLUSIONS

DRB was found to be comparable to clay and $CaCO_3$ with respect to its properties as a filler of an NR vulcanisate. Thus, it should have a high potential for being utilised as such, especially when coupled with the fact that it is cheap as well as renewable.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge Thailand Research Fund (TRF) for a research grant (RDG5150042).

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