

Effect of Defatted Rice Bran, Calcium Carbonate and Clay on Properties of Cellular Natural Rubber

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Abstract

The effects of defatted rice bran (DRB) as a filler for cellular natural rubber (NR) vulcanizate on its cell morphology, water absorption and mechanical properties were investigated. The properties of the DRB-filled cellular NR vulcanizate were also compared with clay-filled and CaCO₃-filled cellular NR vulcanizates at similar loading level (30 parts per hundred of rubber). Scanning electron micrographs revealed that the greater cell size was observed when cellular NR vulcanizates were filled with all types of filler. The DRB-filled cellular NR vulcanizate exhibited better and more uniform dispersion of cellular cell structure as compared to CaCO₃-filled and Clay-filled cellular NR vulcanizates. Moreover, the DRB-filled cellular NR vulcanizate gave the highest water absorption value, tensile strength and 100% modulus as compared to CaCO₃-filled and Clay-filled cellular NR vulcanizates. The elongation at break of DRB-filled cellular NR vulcanizate was found to be comparable to that of CaCO₃-filled cellular NR vulcanizate. However, the cellular NR vulcanizate filled with DRB showed the lowest hardness value. According to these observations, DRB can potentially be used as a cheap and more environment-friendly natural filler for cellular natural rubber.

Key Words: Cellular natural rubber; Defatted rice bran; CaCO₃; Clay; Blowing agent

Introduction

Cellular polymers have been used commercially in a wide range of applications, due to their structural properties, such as light weight, buoyancy, thermal and acoustic insulations, cushioning performance, energy absorption, and impact damping (Zhang and Ashby, 1994; Sims and Bennett, 1998; Ruiz-Herrero et al., 2005; Kim et al., 2007; Wang et al., 2007). Cellular rubber or expanded rubber is based on natural rubber (NR) or synthetic rubbers produced by the use of suitable compounds containing blowing agent. It is a material made up of a rubber matrix and a gas phase (Wimolmala et al., 2009). Fillers are added to rubber compounds for the purpose of reinforcing them and/or cheapening their cost. Carbon black, silica, silicate, and calcium carbonate (CaCO₃) are usually used as fillers in cellular rubber (Lin et al., 2004). Apart from these fillers, the use of renewable

materials such as rice hull ash and defatted rice bran have been used as fillers in cellular rubber (Srilathakutty et al., 2002; Moonchai et al., 2015). Rice hull ash (RHA) can be used as a low cost filler in NBR/PVC based microcellular soles (Srilathakutty et al., 2002). The mechanical properties of the microcellular soles containing silica and RHA were found to be comparable. Defatted rice bran is a by-product of the rice bran oil extraction process. DRB is normally used to reduce the final cost of animal feed or is discarded as agricultural waste (Moonchai et al., 2012). It is sustainable, lightness, biodegradable, and environment-friendly nature. Recently, defatted rice bran (DRB) has also been used as a filler in cellular NR. Moonchai et al. (2015) studied the properties of cellular NR vulcanizate filled with DRB. It was found that the cell size of cellular NR vulcanizate filled with DRB was larger than that of non-filled

cellular NR vulcanizate. The mechanical properties results showed that increasing DRB loading caused an increase in compression set and a decrease in tensile strength and elongation at break of cellular NR vulcanizates. In addition, the DRB-filled cellular NR vulcanizate gave lower offensive odour than that of non-filled cellular NR vulcanizate. This work was aimed to study the effects of DRB on the cell morphology, water absorption, and mechanical properties of cellular NR vulcanizate. The properties of the DRB-filled cellular NR vulcanizate are also compared with clay-filled and CaCO₃-filled cellular NR vulcanizates.

Materials and Preparation of Rubber Compounds

Natural rubber (STR 5L) and all compounding ingredients except for the blowing agent and filler were purchased from Lucky Four Co. Ltd. (Thailand). Oxybis (benzene sulfonyl) hydrazide (OBSH) used as a chemical blowing agent, was purchased from Thai Poly Chemicals Co. Ltd. Dibenzothiozyl disulphide (Vulkacit® MBTS) and tetramethylthiuram disulphide (Vulkacit®TMTD) used as accelerators. Stearic acid and zinc oxide were of rubber grade. Three fillers used were defatted rice bran (DRB), china clay (hydrated aluminium silicate) and ground calcium carbonate (CaCO₃). Clay and calcium carbonate were purchased from Lucky Four Co. Ltd. and DRB was purchased from Thai Edible Oil Co. Ltd. The DRB was passed through an 80-mesh screen and dried in a circulating air oven at 70°C for 17 h before mixing (Moonchai, S. and Moonchai, D., 2013). The formulations of rubber compounds are shown in Table 1. The four compound formulations are designated as No Filler, DRB, clay and CaCO₃. Mixing was carried out in a two-roll mill (model YFTR-8). The obtained rubber compounds were then compression-moulded using a hydraulic hot press (OOMN semi-automatic moulding press model HPC-100(D)) at 150 °C according to their respective cure times (t₉₀). The cure time (t₉₀) was carried out according to ISO 6502 using a moving die rheometer (model UR-2010, U-CAN Dynatex Inc.) at a temperature of 150°C with 3° arc for 60 min.

Table 1 Formulations of rubber compounds

Ingredient	Amount (phr)			
	No Filler	DRB	CaCO ₃	Clay
NR (STR 5L)	100	100	100	100
Sulphur	2.5	2.5	2.5	2.5
Zinc oxide	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0
MBTS	1.0	1.0	1.0	1.0
TMTD	0.5	0.5	0.5	0.5
Aromatic oil	3.0	3.0	3.0	3.0
Lowinox®CPL	1.0	1.0	1.0	1.0
OBSH	6.0	6.0	6.0	6.0
DRB	-	30	-	-
CaCO ₃	-	-	30	-
Clay	-	-	-	30

Characterizations and Properties Testing

Water Absorption

The sample of cellular NR vulcanizates with different types of filler was in a cylindrical disk form, having a diameter of 14 mm and a thickness of 6.4 mm. All specimens were weighed and immersed into the water for 288 h at room temperature to attain the equilibrium water uptake content. The samples were then dried using tissue paper before weighing by electronic balance. The water absorption content (W_c) was measured by percent weight increase in the sample according to eq. (1)

$$W_c = \frac{(W_t - W_o) \times 100}{W_o} \quad (1)$$

where W_t is the weight of the test specimen at a given time t (g), and W_o is the initial weight of the test specimen before placing in water (g).

Mechanical Properties

The tensile properties of cellular NR vulcanizates were determined using an Instron universal testing machine (model 5569, Instron Corp.) with a crosshead speed of 500 mm/min., and 1-kN load cell. The specimens were die-cut from a 2-mm-thick compression-moulded sheet. The dimension of the test specimens used was

type I according to ISO 37. The tensile strength was determined from stress at rupture. The elongation at break and the modulus at 100% strain were also determined.

The hardness of cellular NR vulcanizates filled with different types of filler was determined according to ISO 7619-1 using a Shore A durometer (model HPE-A, Bareiss). The median value of three different positions on each specimens (about 6-mm thick) was reported.

Scanning Electron Microscopy

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

Results and Discussion

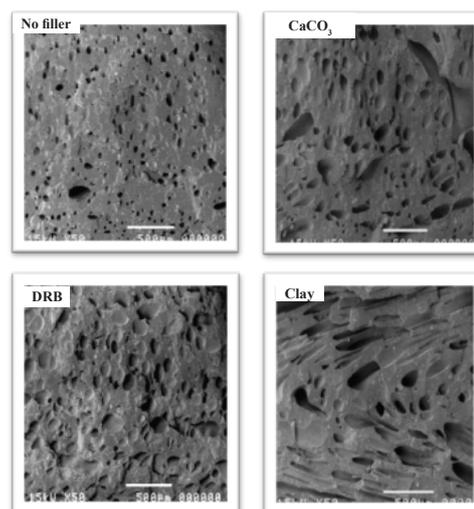
Cell Morphology

Scanning electron micrographs of the fractured surfaces of the cellular vulcanizates filled with different types of filler at 30-phr loading are shown in Figure 1. It was found that the cellular vulcanizates produced by OBSH had closed-cell structures. The greater cell size was observed when cellular vulcanizates were filled with all types of filler. The DRB-filled cellular vulcanizate exhibited better and more uniform dispersion of cellular cell structure as compared to CaCO_3 -filled and clay-filled cellular vulcanizates. Furthermore, it can be clearly seen that the clay-filled cellular vulcanizate showed an irregular shape of cell structure in the NR matrix, with the poorest cell dispersion. Therefore, DRB can be used as a nucleating agent in the expansion process of cellular rubber, resulting in an increase in the cell size with uniform dispersion of cell structure.

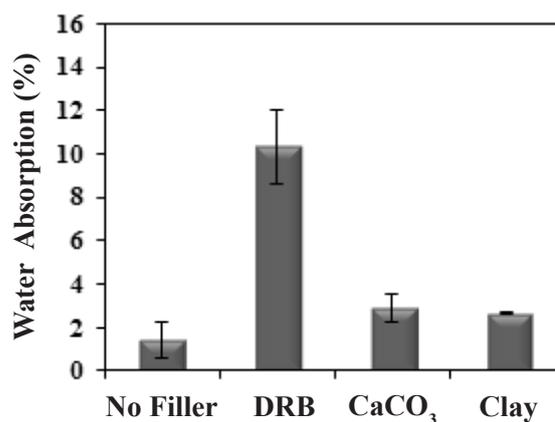
Water Absorption

Figure 2 shows the equilibrium water absorption values of cellular vulcanizates filled with different types of filler. The addition of fillers in the cellular vulcanizates caused an increase in the water absorption values due to the greater cell porosity of filled cellular vulcanizates as compared to non-filled cellular vulcanizate (Figure 1). The DRB-filled cellular NR vulcanizate gave the highest absorption value due to the hydrophilic character

of DRB (Moonchai et al., 2012) and higher number of foam porosity to absorb water. The water absorption value of CaCO_3 -filled cellular vulcanizate was found to be comparable to that of clay-filled cellular vulcanizate.



Figures 1 SEM micrographs of cellular NR vulcanizates filled with different types of filler

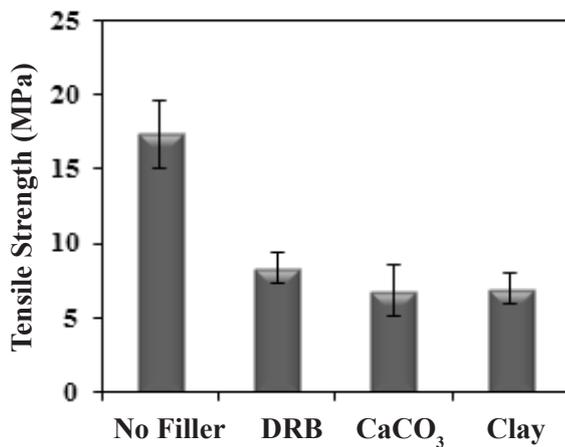


Figures 2 Water absorption of cellular NR vulcanizates filled with different types of filler

Mechanical Properties

The results of the tensile properties of filled cellular NR are depicted in Figures 3-5. The addition of fillers in the NR matrix caused a negative effect on the tensile strength and elongation at break. The tensile strength decreased with the addition of fillers as expected because the rubber matrix phase to resist the tensile force had been replaced by the presence of gas phases (Wimolmala et al., 2009). This result was associated with the cell structures which indicate that the greater cell size gave

the lower strength in the matrix. Moreover, the DRB-filled cellular vulcanizate gave the highest tensile strength as compared to CaCO₃-filled and clay-filled cellular vulcanizates. This is may be due to the DRB-filled cellular vulcanizate exhibited better and more uniform dispersion of cellular cell structure as compared to CaCO₃-filled and clay-filled cellular vulcanizates as shown in Figure 1. The explanation for the changes in tensile strength could also be used to describe the changes in elongation at break. The cellular vulcanizate filled with DRB showed the highest 100% modulus and was comparable to the non-filled cellular vulcanizate, with CaCO₃-filled cellular vulcanizate giving the lowest value (Figure 5). The hardness values of cellular vulcanizates are shown in Figure 6.



Figures 3 Tensile strength of cellular NR vulcanizates filled with different types of filler

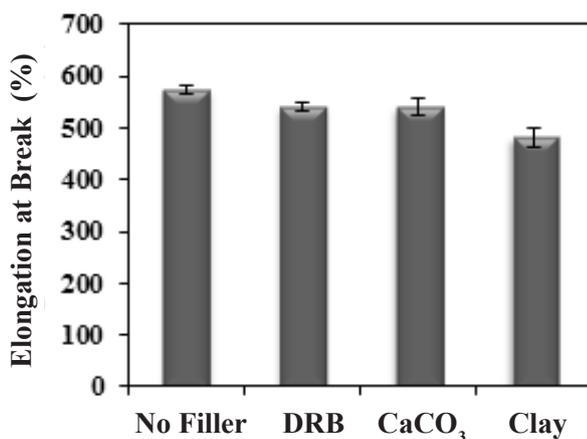


Figure 4 Elongation at break of cellular NR vulcanizates filled with different types of filler

Compared to non-filled cellular vulcanizate, all filled cellular NR vulcanizates exhibited lower hardness values, with DRB-filled cellular vulcanizate giving the lowest value, followed by CaCO₃-filled and clay-filled cellular vulcanizates, respectively. The hardness values are seen to directly correspond to the cell structures (Figure 1), which indicate that the filled cellular vulcanizates showed the greater cell size. The lower hardness of the filled cellular vulcanizates due to the rubber matrix phase had been replaced by the presence of gas phases.

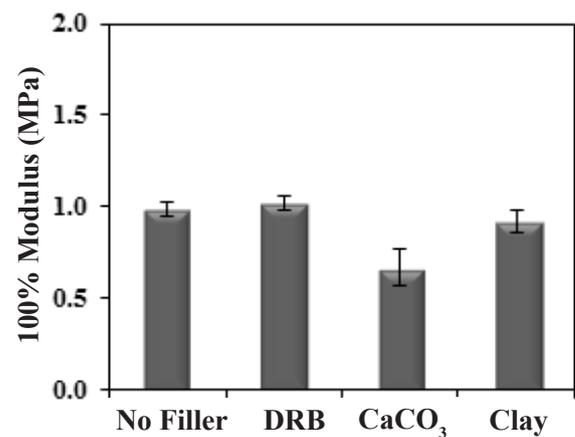


Figure 5 100% modulus of cellular NR vulcanizates filled with different types of filler

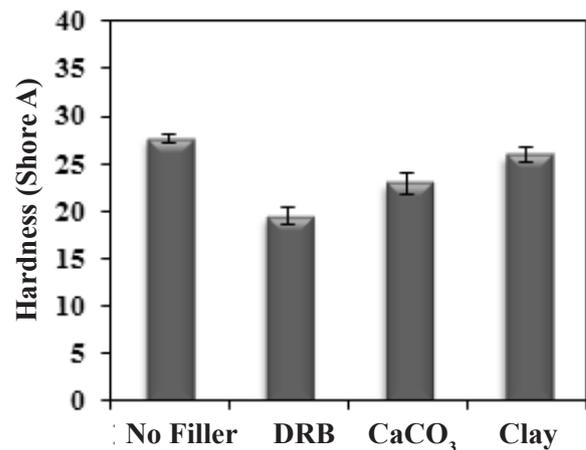


Figure 6 Hardness of cellular NR vulcanizates filled with different types of filler

Conclusion

This study explored the use of DRB as a filler in cellular NR vulcanizate. The properties of the DRB-

filled vulcanizate were compared with clay-filled and CaCO₃-filled vulcanizates. DRB can be used as a nucleating agent in the expansion process of cellular rubber and exhibited better and more uniform dispersion of cellular cell structure as compared to CaCO₃-filled and clay-filled cellular NR vulcanizates. Moreover, the vulcanizate filled with DRB showed highest water absorption value and tensile strength, while it gave elongation at break comparable to that of CaCO₃-filled cellular vulcanizate. Compared to non-filled cellular vulcanizate, the filled vulcanizates exhibited lower hardness values, with DRB-filled cellular vulcanizate giving the lowest value, followed by CaCO₃-filled and clay-filled cellular vulcanizates, respectively.

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