Mechanical Properties of Natural Rubber Composites Filled with Starch Sludge Compared with Other Waste and Commercial Fillers

Duangkamol Dechojarassri, Narumon Ratikant, Siriphat Charoenrat, and Panu Danwanichakul

***Abstract*—Mechanical properties of natural rubber composites filled with waste materials including waste tire rubber, rice husk ash and starch sludge were comparatively investigated along with commercial reinforcing fillers, carbon black and silica, using maleated natural rubber (MNR) or silane (Si69) as a coupling agent. It was found that rubber with rice husk ash gave higher tensile strength than ones with starch sludge and waste tire. Rice husk ash gave similar strength to silica and using MNR was better than Si69. Waste fillers gave higher compression set than carbon black and crumb rubber yielded better abrasive resistance than carbon black and silica. It was also seen that mechanical properties decreased with increasing starch sludge loading. The optimum loading is 10 phr starch sludge with 5 phr MNR. These experimental results showed that for certain applications, waste materials could be used as alternative filler in the rubber production.**

***Index Terms*—Rice husk, rubber composite, starch sludge, waste tire.**

I. Introduction

Thailand is one of top three natural rubber producers in the world but the rubber usage in the country is less than what expected by the government because it is more expensive than synthetic rubber. To promote an increase in usage of domestic natural rubber could, therefore, help stabilize the rubber cost in the market. One of the promising methods to reduce the production cost nowadays is using low-cost fillers together with a cheap vulcanizing system. On one hand, carbon black and silica are widely used as commercial reinforcing fillers for the production of natural rubber products and some other polymers. On the other hand, calcium carbonate is considered as inexpensive filler to increase volume of the final rubber products and thereby reducing the cost of production. Low-cost fillers possessing the reinforcing properties would be interesting choices for rubber production in this aspect.

Manuscript received December 19, 2016; revised May 5, 2017.

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The idea of using waste materials as fillers in rubber composites has been attracting many researchers for a very long time. For example, eggshell in micron sized particles together with carbon black was added to increase mechanical strength of the composites [1]. As a method to get rid of waste tire rubber, it was made into small granules and added as filler in the new rubber compound [2]. Agricultural waste also gained much attention, for instance, lignin [3] or softwood-lignin [4], short pineapple leaf fibers [5] and rice husk ash (RHA) [6] were added as fillers into the rubber composites. In addition, plastic wastes were also blended to rubber compound such as ethylene-vinyl acetate (EVA) [7] and waste poly amide [8].

As studied in the old systems of commercial fillers, the interaction among filler particles and rubber matrix is always the main concern in the mixing process since natural rubber is highly hydrophobic. Addition of hydrophilic particles such as silica is expected to yield poor mixing with rubber. To solve the problem of immiscibility between these materials, a compatibilizing agent or coupling agent is needed. One of the common coupling agent is a group of silane coupling agent. However, grafting rubber molecules with maleic anhydride to increase polarity in rubber molecules and using the grafted-rubber as a coupling agent proved to increase compatibility among rubber and paper sludge [9]. Therefore, maleated natural rubber (MNR) [10] could be a promising coupling.

However, each research work used different formulation in the mixing process so it was difficult to compare the efficiency of those wastes as filler in the rubber composites. In order to compare the efficiency of some wastes as filler, they need to be investigated in the same vulcanizing system, i.e. same rubber formulation during the mixing process. This research focuses on a study of using waste materials including waste tire rubber (waste tire granules), rice husk ash (RHA) from a rice mill and starch sludge from a modified-starch factory. These materials are composed of carbon and/or silica which should enhance the mechanical properties of natural rubber composites so they were later called alternative filler throughout the text. Furthermore, this could increase the value of these waste materials and starch sludge. The objectives of this study are to compare the mechanical properties of rubber filled with different alternative fillers with those of commercial fillers and without or with some amount of MNR or Si69 as a coupling agent which boost compatibility between filler and rubber matrix and also to evaluate the effect of starch sludge loading with different amount of MNR and Si69 on mechanical properties.

doi: 10.18178/ijcea.2017.8.3.658

II. Experimental Procedure

A. Materials

STR 5L grade natural rubber was supplied by Rubber Estate Organization. Silica, stearic acid, and zinc oxide were provided by Loxley Co., Ltd. Waste tire granules or crumb rubber (7, 10 and 30 mesh) was bought from Union Pattanakit Co., Ltd, Starch sludge was obtained from Siam modified starch Co.,Ltd while rice husk ash (RHA) was provided from Pathum Rice Mill Co., Ltd. Tetramethylthiuram disulfide (TMTD) and Si-69 (bis-(3-triethoxysilylpropyl)tetrasulfane) was given by JJ-Degussa Chemicals Ltd. N-Cyclohexyl-2-benzothiazole sulfonamide (CBS) by Sunny World (1989) Co. Ltd. Carbon Black (N330) was purchased from Loxley Co., Ltd and sulfur was purchased from Suksaphan Panich.

B. Fillers Preparation

Starch sludge was dried in an oven at 100˚C for 20 h and then ground with a ball-mill to a powder form. The particles were then sieved to separate particles less than 75 micrometer from those larger than 75 micrometer. The same method was done for rice husk ash.

C. Preparation of Maleated Natural Rubber (MNR) as a Coupling Agent

Maleated Natural Rubber was prepared by blending natural rubber with 5 phr of maleic anhydride in an internal mixer, Brabender. The natural rubber was first dried in an oven at 40˚C for 24 h. The internal mixer was then used to masticate the rubber at 135˚C with a rotor speed of 60 rpm. The mixing was continued for 8 min.

D. Mixing Procedure

Typical rubber formulation used in this research is provided in Table I.

TABLE I: Rubber Composite Formulation

Materials	Composition (phr*)
STR 5L	100
Stearic acid	1
Zinc Oxide	5
CBS	0.5
TMTD	0.1
Fillers	30
Si-69**	2.4
Sulfur	2.5

*phr stands for parts per hundred parts of rubber
**Used only with rubber filled with RHA and silica

Mixing was carried out in the Brabender at 50˚C with a rotor speed at 40 rpm. Mixing was a two-staged process. At the first stage, rubber was masticated for 3 min and then mixed with fillers for 2-4 min depending on the type of fillers. Subsequently, stearic acid and zinc oxide were filled and mixed together for 3 min and then the rubber was rolled with a two-roll mill and cut for the next stage. At the second stage, the rubber from the first stage was mixed with CBS, TMTD and sulfur at 55˚C for 2 min, rolled with the two-roll mill and a piece of rubber was cut for testing the cure characteristics at Rubber Research Institute (Thailand). Finally, the rubber was molded in different shapes appropriate for different mechanical property test.

Stearic acid and zinc oxide were used as activators. CBS and TMTD were used as accelerators. The fillers used were carbon black (CB), silica (Si), crumb rubber of size 7 mesh (2.8 mm) (CR 7M), 10 mesh (1.65 mm) (CR 10M), and 30 mesh (0.54 mm) (CR 30M), rice husk ash of mixed sizes (RHA), rice husk ash of mixed sizes with Si69 (RHA+Si69), rice husk ash of mixed sizes with MNR (RHA+MNR), rice husk ash of size less than 75 microns (RHA<75), rice husk ash with size less than 75 microns with Si-69 (RHA<75+Si69), rice husk ash with size less than 75 microns with MNR (RHA<75+MNR), starch sludge (SS), starch sludge with Si69 (SS+Si69), and starch sludge with MNR (SS+MNR).

E. Mechanical Properties Testing Surface Hardness

Samples were tested with dead load hardness tester, shore A, at room temperature according to ASTM D 2240.

1) Tensile strength

According to ASTM D412, dumb-bell shaped samples were cut from the molded sheets, die C, which is 25 mm of gauge length and tested by using the universal testing machine (UTM). The test sample looks as shown in Fig. 1.

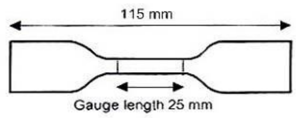

Fig. 1. Dumb-bell shaped sample.

2) Compression set

Cylinder shaped samples were cut, with 1.25 cm thickness and 3 cm diameter as shown in Fig. 2.

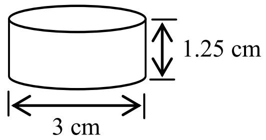

Fig. 2. Compression-set samples.

According to ASTM D 395-89, the sample was put between metal sheets of tester. The compression tester had spacer bars for setting a distance of compression. The sample was compressed so that the thickness decreased about 25% from the origin and then the tester along with the sample was aged in an oven at 100◦C for 22 h. The sample was later taken out of the tester and held at room temperature. The thickness of the sample was measured and %compression set can be calculated according to Eq. (1).

$$\% C_B = [(t_0 - t_1)/(t_0 - t_n)] \times 100 \quad (1)$$

Here, % C_B is the percentage of compression set, t_0 is the thickness of the sample before aging (mm), t_1 is the thickness of the sample after aging (mm) and t_n is the thickness of space bars (mm).

3) Abrasion resistance

Samples were cut in cylindrical shape with its length and diameter of 2.5 and 1.2 cm, respectively. Testing method is according to DIN 53516. The volume losses (mm^3) could be calculated by using Eq. (2).

$$\text{Volume loss} = \Delta m \text{ x } S_0/(\text{density} \times S) \qquad (2)$$

where, Δm is weight loss, S_0 is abrasion power. In this case S_0/S was set to 10/9.

4) Scanning electron microscopy (SEM)

The samples were cracked in liquid nitrogen. The cracked surface was examined by SEM (Jeol JSM 6301F) at MTEC.

III. Results and Discussion

To clarify the effect of fillers on mechanical properties of the rubber composites, one may follow previous research works and compare the results. However, it is very difficult to do so since each research work applied different formulation of the effective chemicals including vulcanizing agents and fillers, thereby yielding different vulcanizing systems. The mechanical properties of rubber composites are dependent on the degree of vulcanization which may be considered as a chemical crosslink and the type of vulcanizing system as well as the degree of physical crosslink between rubber molecules and filler particles. Therefore, to compare the effect of fillers, the effect of vulcanizing systems should be avoided. To that end, in this work all experiments using waste fillers and commercial adopted the same rubber formulation as shown in Table I.

A. Tensile Properties

The universal testing machine was used to obtain tensile properties including tensile strength, the maximum tensile stress the rubber sample can withstand before being drawn to break, and elongation at break showing the elasticity of the sample through the maximum length of the sample being breaking.

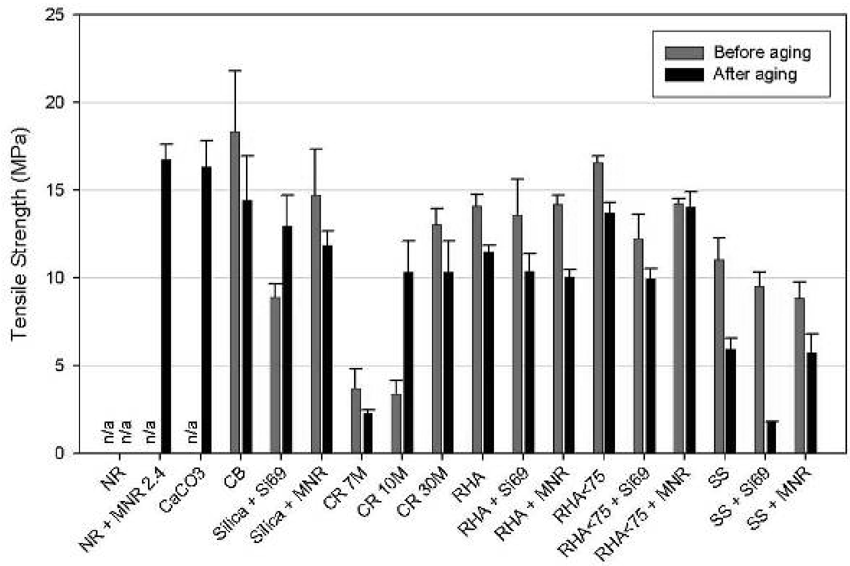

Fig. 3. The effect of various fillers on tensile strength.

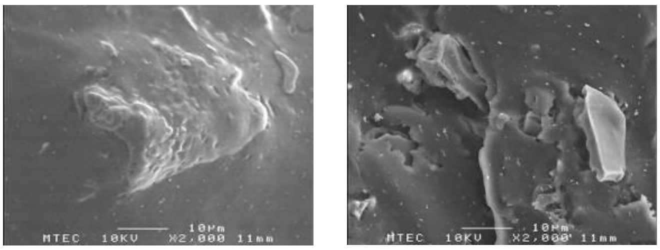

Fig. 4. SEM micrograph of rubber filled with (a) RHA <75+ MNR 2.4 phr or (b) RHA<75 + Si69 2.4phr.

Fig. 3 shows the comparison between each rubber filled with various fillers. It was found that the rubber filled with carbon black has a highest tensile strength at 18 MPa. Rubber filled with rice husk ash has tensile strength close to that filled with silica, but greater than rubber filled with starch sludge and crumb rubber, respectively. However, it should be noted that the smallest size of crumb rubber (CR 30M) yielded high tensile strength comparable to rice husk ash. The small size of filler is one of important factors in strengthening the interaction between rubber and filler. As the size decreases, the area per unit volume of the particle increases resulting in strong attractive interactions among particles and rubber molecules. As can be seen also from Fig. 3, rice husk ash with smaller size gave better tensile strength.

Considering the use of coupling agents, it was unexpectedly seen that rubber without coupling agent was better than that with coupling agent, likely attributable to poor mixing process. However, MNR seemed to be a better coupling agent than Si69.

Fig. 4 shows that the compatibility between rubber-filler was improved by using MNR. The particles were better mixed into the rubber matrix because they could be more effectively distributed in the matrix, not aggregated into larger particles.

Fig. 5 shows the effect of starch sludge loading in rubber. It was obviously seen that tensile strength decreased with increasing starch sludge loading both in the case of using and not using NMR. As the amount of filler was increased, the filler particles or aggregates were no longer separated or wetted by rubber matrix. So the reduction in tensile strength might be due to the agglomeration of filler particles [6].

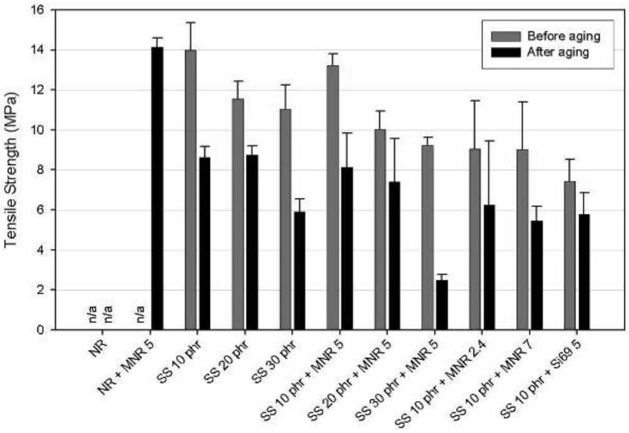

Fig. 5. The effect of starch sludge loading on tensile strength.

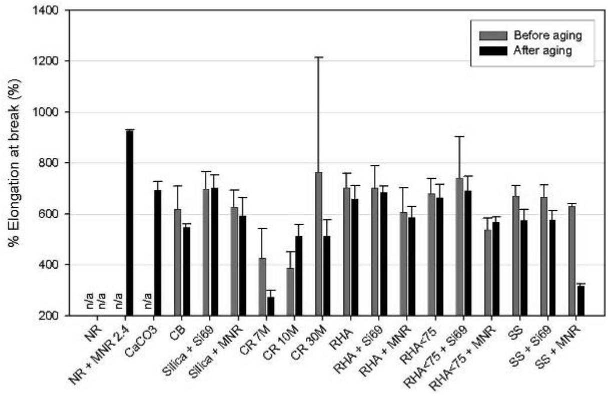

Fig. 6. The effect of various filler on %elongation.

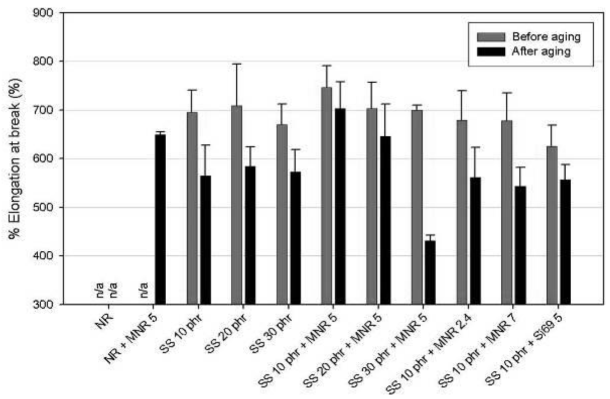

Fig. 7. The effect of filler loading on %elongation.

Elongation at break reflecting the elastic property of rubber vulcanizates is shown in Fig 6. It was found that the rubber filled with carbon black elongated at break point less than that with silica. The rubber filled with rice husk ash again showed elongation at break close to that with silica, and greater than those with starch sludge and crumb rubber. Similarly, crumb rubber of the smallest size (CR 30M) gave very good elongation at break which is nearly 700%.

Fig. 7 shows the elongation at break for rubber filled with different starch sludge loading. It can be seen that MNR could improve elastic properties of rubber and with increasing loading the elastic properties seemed to decrease. The optimum formula was rubber filled with 10 phr of starch sludge and 5 phr of MNR which gave the highest elongation.

B. Surface Hardness

The surface hardness of the rubber filled with commercial fillers was 38-42 shore A, whereas for those filled with crumb rubber it was 38-45 shore A and for those filled with rice husk ash and starch sludge it was in the range of 40-50 shore A. In addition, the surface hardness decreased with increasing starch sludge loading.

C. Compression Sets

Higher percentage of compression set represents lower resilient properties. The compression set of rubber filled with commercial fillers was 40%. For alternative filler, percent of compression set was in the range of 40-50%. The rubber-filler composite with MNR as coupling agent yielded less compression set than rubber-filler composite coupled with Si69.

D. Abrasion Resistance

The volume loss was obtained during abrasion test. More loss represents less abrasion resistance. It was noted that the rubber filled with crumb rubber had 20-35 mm^3 of volume loss, lower than those of rubber filled with commercial filler and unfilled rubber, showing a promising application that needs abrasion resistance.

IV. Conclusion

The mechanical properties of natural rubber composites filled with waste materials and starch sludge compared with commercial fillers were investigated. The results showed that rice husk ash seemed to be the promising alternative filler to silica and that starch sludge and crumb rubber had adequate mechanical properties for certain appropriate applications, provided that the particle sizes are very small. The rubber filled with waste materials could improve compression set of rubber compound, better than the commercial silica but still lower than carbon black. The weight losses of rubber composites filled with waste tire particles during abrasion tests were the least among all samples especially when compared with silica. With suitable applications, waste materials could be used as inexpensive filler in the rubber products.

Acknowledgment

We are grateful to The Cleaner Technology Internship Program, Thammasat University Node for funding and to the Department of Chemical Engineering and the Department of Industrial Engineering, Faculty of Engineering, Thammasat University for essential equipment. We also appreciate assistances from Rubber Research Institute (Department of Agriculture), Rubber Estate Organization, Siam Modified Starch Co., Ltd, Pathum Rice Mill Co., Ltd, and Loxley Co., Ltd.

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