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Fillers Derived from Plantation Produces: Role of Rice Husk Ash in Rubbers

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ABSTRACT

Rice husk ash (RHA) obtained from partial combustion of paddy haystack is known as filler in various applications including as in rubber composition. The richness of silica in it has made such compositions more interesting and useful in respect of sustainability in preference to fillers from fossil fuels. In this study, a salient account on RHA in NR (CV 60) and ethylene propylene diene monomer (EPDM) composites are presented. The NR-based compositions offered a stable set of properties. The scanning electron microscopy (SEM) fractography shows that the mode of failure is mixed, that is cohesive, at the interface. The fibrous fillers remain embedded in the rubber matrix. In case of EPDM composites, the tensile properties did not show much change. However, the SEM fractrographs did not exhibit signs for matrix-filler separation. On the contrary, the failure was prominently in cohesive mode as confirmed by the presence of flow lines.

Key words: *White rice husk ash, Black rice husk ash, Natural rubber, Ethylene propylene diene monomer.*

1. INTRODUCTION

Nowadays, increasing awareness about depletion of fossil fuels has led to looking for alternate sources. The alternate source could be silica based fillers. However, in this case, cost and mixing parameters entirely change, resulting in heavy price of the finished products even though the finished products have good properties. Likewise, environmental concerns must also be taken into account. This problem leads to several solutions such as the use of marble sludge, rice husk ash (RHA) [1], and rice bran. RHA has been used as filler and studied for its role in rubber reinforcement in terms of tensile and tear properties for some time [2-7]. They are abundant in nature as India is generally an agricultural country. Rice milling generates a by-product known as husk. This surrounds the paddy grain. During milling of paddy, about 78% of weight is received as rice, broken rice, and bran. Rest of 22% of the weight of paddy is received as husk. This husk is used as fuel in the rice mills to generate steam for the parboiling process. This husk contains about 75% organic volatile matter, and the balance 25% is converted into ash during the firing process, and it is known as RHA and its generic composition is given in Table 1. This RHA in turn contains around 85-90% amorphous silica. Hence, for every 1000 kg of paddy milled, about 220 kg (22%) of husk is produced, and when this husk is burnt in the boilers, about 55 kg (25%) of RHA is generated. India is a major rice producing country, and the husk generated during milling is mostly used as a fuel in the boilers for processing paddy, producing energy through direct combustion, and/or by gasification. About 20 million tons of RHA is produced annually. This RHA is a great environment threat causing damage to the land and the surrounding area in which it is dumped. Many ways are being thought of disposing them by making commercial use of this RHA.

The two forms of RHA contain carbon and silica which are otherwise known for their role as fillers in rubber [8-10].

2. EXPERIMENTAL

Elastomers, commonly available as NR CV 60 (natural rubber of constant viscosity, 60) and ethylene propylene diene monomer (EPDM), were used. The organic filler RHA was obtained from Astra chemicals, Chennai (white RHA), and Kothari bio fuels Ltd., (black RHA), Chennai. Other additives used were FEF, SRF, and HAF carbon blacks. ZnO (zinc oxide), stearic acid, 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), aromatic oil, paraffinic oil, n-cyclohexyl-2-benzothiazole sulfinamide (CBS), tertramethylthiuram disulfide (TMTD), and sulfur were used as available in standard rubber laboratory.

The compounding formulations are given in Tables 2 and 3. It consists of normal ingredients such as TMQ as antioxidant, stearic acid, ZnO as activators, and

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sulfur as the vulcanizing agent while CBS as the accelerator. HAF carbon black is used as the primary reinforcing filler while the process oil is aromatic oil which is added up to 5 phr for 30 phr of HAF black. The control compound contains HAF only and used for comparison with the RHA-filled compounds. The master batch without the accelerators and curatives was mixed in kneader (capacity 1 l) for 30 min, and then, final batch was produced as a sheet out in the laboratory size two roll mill.

The compounding consists of FEF carbon black which is the primary reinforcing filler, and RHA was added subsequently to the rubber followed by paraffinic oil as process enabler. The accelerator and vulcanizing agents used are CBS, TMTD, and sulfur. The RHA was added to the rubber in the level of 10, 20, and 30 phr. The master batch without the accelerators and curatives was mixed in kneader for 30 min, and then, final batch was produced as a sheet out in the two roll mill open mixer.

3. MOONEY SCORCH TEST

The scorch test was conducted using Ektron Mooney viscometer, and the test temperature used was 135 and 145°C. From the test, it is found that black RHA compounds were sensitive than control and white RHA compounds in terms of the onset of incipient cross-linking (Figures 1-4).

Here, it is found that RHA at increased addition decreases the scorch safety in NR compounds. The decreased safety was found to be more than the gain in the minimum viscosity. The cross- over of cure rate in black RHA at 20 phr is noteworthy (Figures 5-8).

Here, the pattern was little different in 20 phr addition of WRHA that presented better scorch safety. However, in BRHA, increased addition reduced scorch safety.

Table 1: Chemical composition of RHA.

Chemical composition %	White RHA	Black RHA
Calcium oxide	0.1	0.1
Magnesium oxide	0.4	0.2
Ferrous oxide	0.1	0
Potassium oxide	1.6	1.1
Sodium dioxide	1.6	1.1
Aluminum oxide	Trace	Trace
Phosphorus pent oxide	Trace	Trace
Silica	96.2	54.1
Carbon	1.6	44.5

RHA=Rice husk ash

Table 2: Preparation of NR compounds.

Ingredients	Phr
NR CV 60	100
TMQ	1.5
ZnO	1.5
Stearic acid	3
HAF carbon black	30
RHA (white and black)	0, 10, 20, 30
Aromatic oil	5
CBS	1.5
Sulfur	1.5

TMQ=2,2,4-trimethyl-1,2-dihydroquinoline, CBS=n-cyclohexyl-2-benzothiazole sulfinamide, RHA=Rice husk ash

4. RESULTS AND DISCUSSION

Tensile properties were studied and analyzed for the vulcanizates. The properties are represented in the charts as shown in Figures 9-11.

The 10 phr BRHA containing NR vulcanizate had better tensile strength and elongation at break. The scanning electron microscopy (SEM) fractography shows that the BRHA interacted well with the matrix (NR), and thus resulting in better tensile, but for the microlevel impurities such as unburned husk fibers, the properties could have been better. The matrix failed mostly through cohesive mode with occasional failure at the interface of the rubber-RHA.

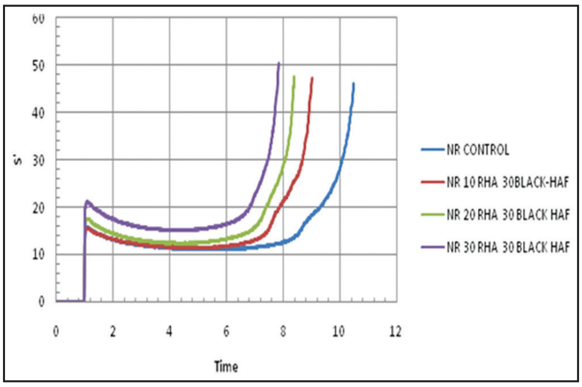

Figure 1: NR CV 60 with WRHA at 135°C.

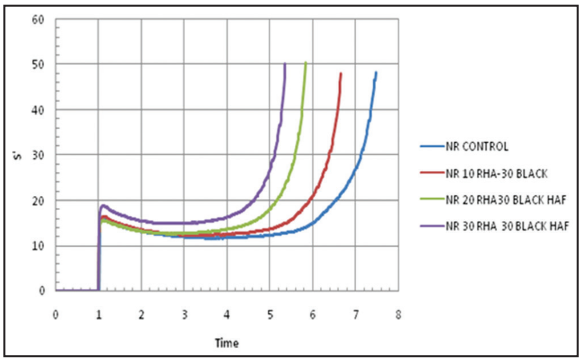

Figure 2: NR CV 60 with WRHA at 145°C.

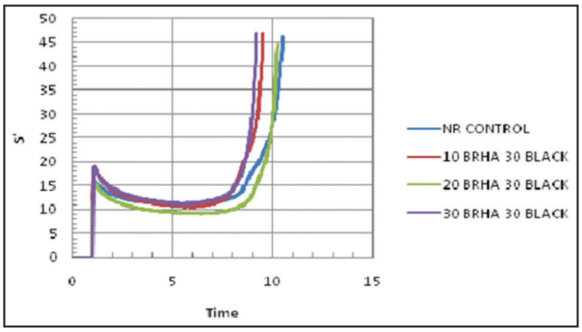

Figure 3: NR CV 60 with BRHA at 135°C.

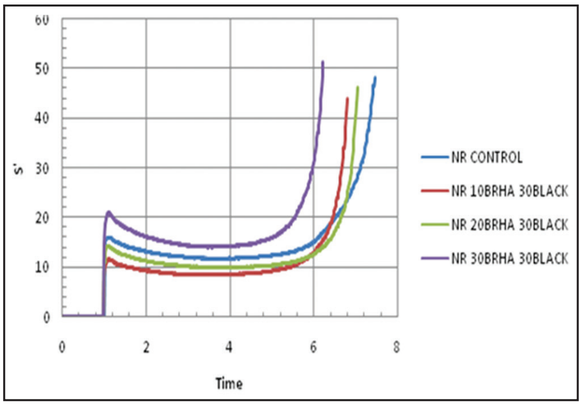

Figure 4: NR CV 60 with BRHA at 145°C.

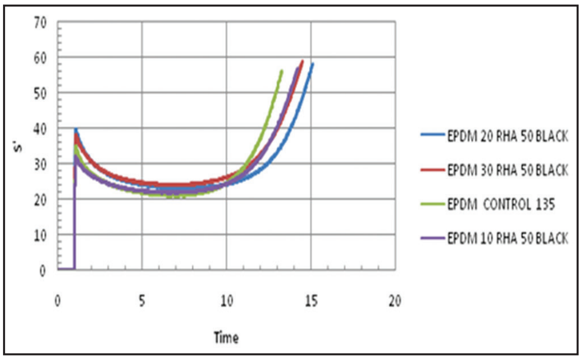

Figure 5: Ethylene propylene diene monomer with WRHA at 135°C.

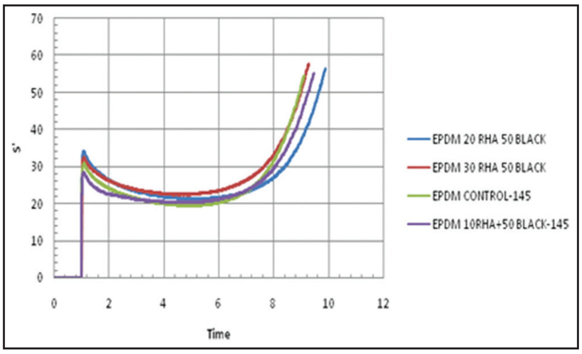

Figure 6: Ethylene propylene diene monomer with WRHA at 145°C.

Here, in the above fractography (Figure 12), there is a depiction of flow lines in the cured compound

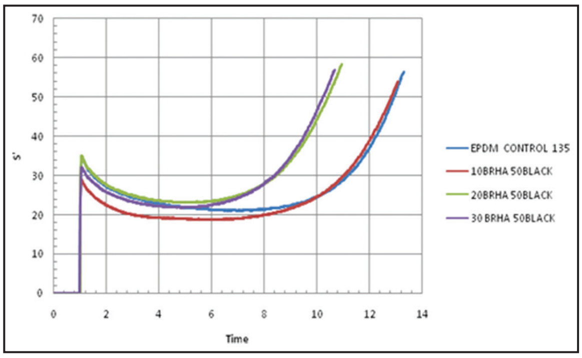

Figure 7: Ethylene propylene diene monomer with BRHA at 135°C.

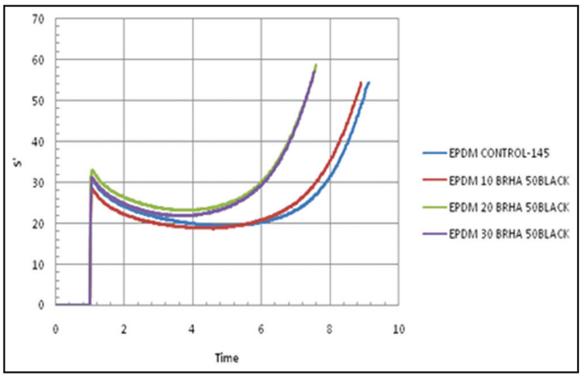

Figure 8: Ethylene propylene diene monomer with BRHA at 145°C.

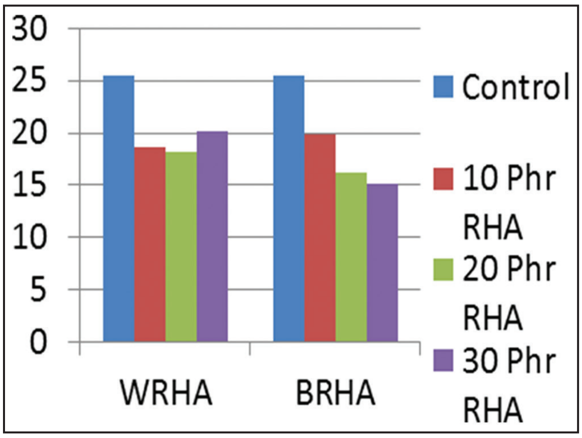

Figure 9: NR CV 60, tensile strength.

which has weakened the elastomers itself. This flow line was a result of increased addition of BRHA that would have caused extensive cross-linking before the intermingling of the flow fronts. However, certain portions indeed depict that the tensile elongation was good since it had micro elongations.

Comparing the tensile strength and corresponding elongation at break, it is easily depicted that the white RHA vulcanizates showed medium elongation with better tensile properties, whereas the black RHA compound showed too much of elongation similar to the control compound but with increased BRHA addition

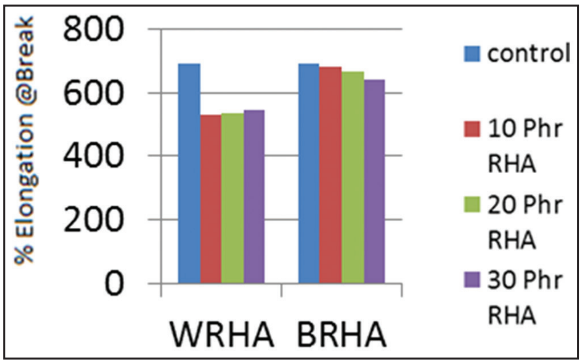

Figure 10: NR CV 60, EB%.

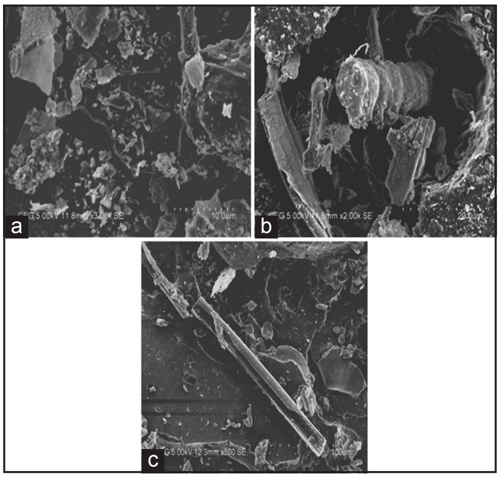

Figure 11: Scanning electron microscopy fractography for NR vulcanizate with 10 phr of BRHA.

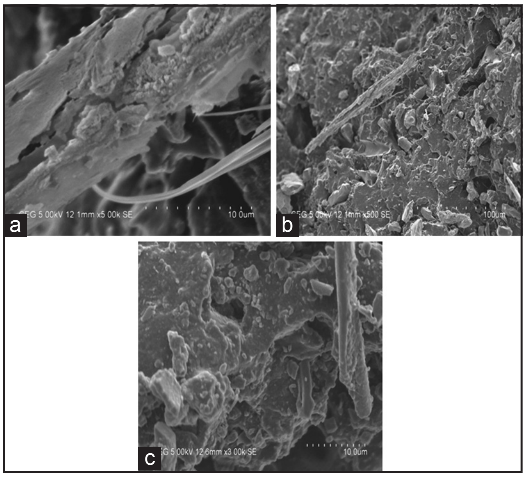

Figure 12: (a-c) Scanning electron microscopy fractography of NR with 30 BRHA.

the properties began to reduce to around 15 MPa. While with WRHA compound, increased addition of filler resulted in better properties but not equal to the control compound around 20 MPa in NR compound containing 30 phr WRHA (Figures 13 and 14).

Addition of RHA in EPDM exhibited different results compared to NR CV 60, with medium elongations and medium tensile strengths. The SEM fractography showed cohesive failure of the cured sample. Flow lines were noticed, especially in increased BRHA addition to the elastomers (Figures 15 and 16).

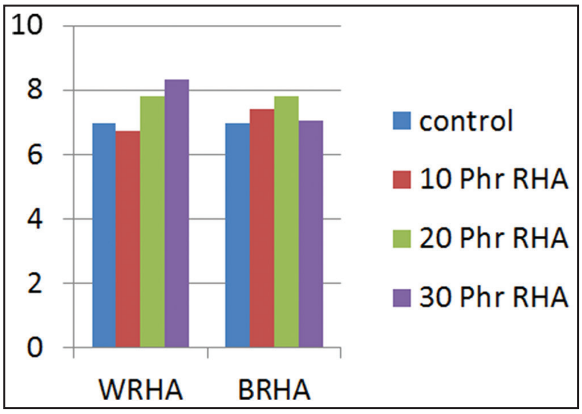

Figure 13: Tensile strength of ethylene propylene diene monomer composites.

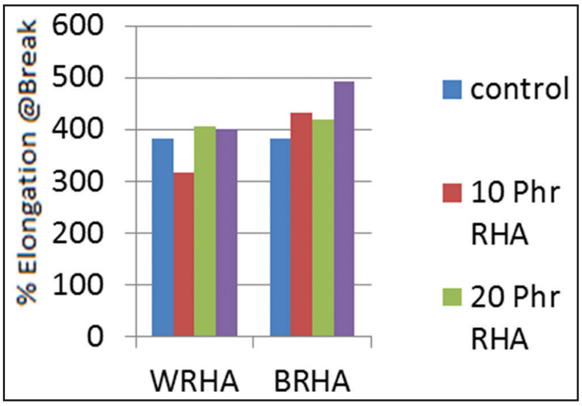

Figure 14: Elongation of ethylene propylene diene monomer composites.

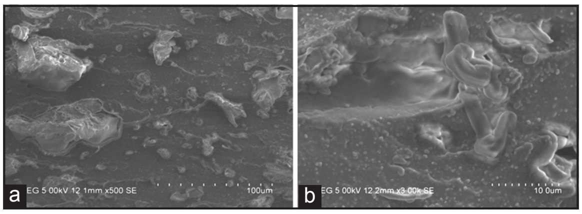

Figure 15: (a and b) Scanning electron microscopy fractography of ethylene propylene diene monomer with 10 BRHA.

The flow lines were observed in BRHA compounds for both NR CV 60 compounds and EPDM compounds. In the SEM images, flow lines were prominent confirming cohesive failure. Undispersed filler particles were not visible.

5. CONCLUSION

The use of RHA as a filler in elastomers showed different results in each elastomer used. It increased

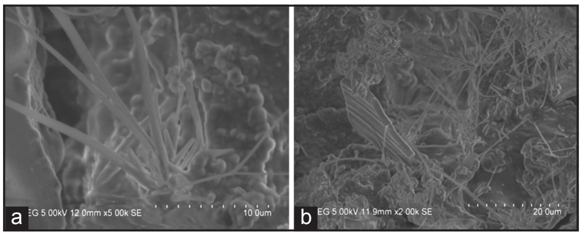

Figure 16: (a and b) Scanning electron microscopy fractography of ethylene propylene diene monomer with 30 BRHA.

Table 3: Preparation of EPDM compounds.

Ingredients	Phr
EPDM	100
FEF	50
RHA (white and black)	0, 10, 20, 30
Paraffinic oil	30
ZnO	2
Stearic acid	2
CBS	1.5
TMTD	1.5
Sulfur	1.5

EPDM=Ethylene propylene diene monomer, TMTD=Tertramethylthiuram disulfide, CBS=n-cyclohexyl-2-benzothiazole sulfinamide, RHA=Rice husk ash

the elongation at break for natural rubber compound at the same time provided brittle tensile and tear failure in chloroprene compounds. While in EPDM compounds, it showed poor-to-medium elongation at break with medium tensile properties. The increased addition of RHA caused loss of some elastomer properties in chloroprene compounds. At the same time, it hastened cross-linking and this may be due to certain chemical reaction that could have occurred due to impurity content in the RHA. Further studies could be carried out to optimize the properties.

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