Studies on Physical Chemistry of Rubber-Rice Husk Ash Composites

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Abstract: Nowadays an alternate source of filler from renewable and plant derivatives are being thought of in rubber industries due to their reliability, environmental and economic benefits. Rice Husk Ash (RHA) a byproduct of the rice milling industry is obtained on partial and as well as full combustion of the rice husks. This ash is a good source of silica, silicates and needle shaped carbon and hence can be used as filler for cements. In the present study, a detailed investigation was carried out to understand the RHA as reinforcing material using mechanical properties and fractography using SEM. The rubbers studied were natural rubber (NR), poly chloroprene (CR) and ethylene propylene diene monomer (EPDM). Interestingly, the RHA added NR stock on open mill mixing generated considerable amount of static charges. The properties of NR were found to be as good as regular formulations. EPDM compounds behaved well during mixing. But the properties were found to be poor. CR- RHA compounds were found to result in higher viscosity and the properties were not as good. The SEM studies showed surprisingly cohesive failure as evidenced with the presence of flow lines and the fibrous filler (RHA) remains embedded in the matrix regardless of the chemistry of the repeating unit, NR, EPDM and the chlorine containing monomer in CR.

Keywords: Rice husk ash; rubber; composites; natural rubber; polychloroprene rubber; EPDM; Mooney Scorch; SEM fractography

1 Introduction

Fillers are ingredients at micro to macro level, maybe in powder form or else fibers that are widely used in rubbers in order to smoothen product manufacturing and to enhance properties in terms of tear and abrasion properties. Conveniently, these fillers are classified as reinforcing and extending (non-reinforcing) based on their effect. Mostly, the non-reinforcing fillers are added in higher volume fraction as they yield rubberiness with moderate set of properties. As a result, the rubber compound cost per unit price is much reduced. Particulate and fibrous fillers (in some cases with surface treatments) are used in definite proportion (volume fraction) in order to achieve designer formulations. As on date, carbon black (mostly furnace processed and ASTM grades) and silica (precipitated or hydrated in combination with silane coupling agents) are used. But, these filler, even though highly promising in terms of their reinforcement of cross linked rubber, are becoming unsustainable as the raw materials are becoming scarce and/or the process requires energy intensive operation.

Fortunately, fillers from renewable sources particularly from the plant derivatives available abundantly are being explored as rubber fillers. The morphology of these fillers fills the gap between particulate and fibrous characteristics. As a result, the anisotropic behavior of such filled cross linked rubbers provide rich source of scientific investigation and potential application. Rice husk ash is used in the present investigation as filler in influencing the chemistry of cross linking (scorch), mechanical properties and the fracture behavior of rubbers.
2 Rice Husk Ash

Rice milling generates a byproduct known as husk. This surrounds the paddy grain. During milling of paddy about 78% of weight is received as rice, broken rice and bran. The rest 22% of the weight of paddy is received as husk. This husk is used as fuel in the rice mill in the parboiling process. This husk contains about 75% organic volatile matter and the balance 25% of the weight of this husk is converted into ash and it is known as rice husk ash (RHA). This RHA contains around 85%-90% amorphous silica. So for every 1000 kgs of paddy milled, about 220 Kgs (22%) of husk is produced, and when this husk is burnt in the boilers, about 55 Kgs (25%) of RHA is generated. India is a major rice producing country and about 20 million tons of RHA is produced annually. The RHA of Blaine number close to 3600 (as compared to 3000 for cement; larger the number, finer the powder) can pose environmental pollution if it is not used and one such out let was found to be its role as filler in rubber. Goodyear Tyres announced plans to use rice husk ash as a source for tire additive perhaps for silica. The white husk ash predominantly contains amorphous silica and the black contains about 52% of carbon black. Regular carbon black (furnace type for example) conforms to standards in terms of particle size, structure and the surface chemistry. The black RHA resembles that of GPF (general purpose furnace grade). The typical composition is given in Tab. 1.

The physical properties as compared to carbon black and silica are given in Tab. 2. RHAs are much coarser than the regular reinforcing fillers as shown in the Fig. 1. On grinding the RHA gets finer as shown in Fig. 2.

| Chemical composition (%) | White rice husk ash | Black rice husk ash |
|--------------------------|---------------------|---------------------|
| Calcium oxide            | 0.1                 | 0.1                 |
| Magnesium oxide          | 0.4                 | 0.2                 |
| Ferrous oxide            | 0.1                 | 0               |
| Potassium oxide          | 1.6                 | 1.1                 |
| Sodium oxide             | 0.1                 | 0.1                 |
| Aluminum oxide           | trace               | Trace               |
| Phosphorus pentoxide     | trace               | Trace               |
| Silica                   | 96.2                | 54.1                |
| Carbon black             | 1.6                 | 44.5                |

| Physical properties | Wrha | Brha | Silica | Carbon black |
|---------------------|------|------|--------|--------------|
| Mean particle size(µ) | 5.54 | 2.4  | 0.011-0.019 | 0.026-0.030 |
| Surface area(m²/g)   | 1.4  | 26.4 | 170    | 98.9         |
| Density(g/cm³)       | 2.2  | 1.8  | 2.2    | 1.8          |
Figure 1: White rice husk ash

Figure 2: Black rice husk ash

Figure 3: (a) Rice bran, (b) Rice Husk Ash (c) Rice Husk Ash ground

3 Experimental Work
3.1 Materials Used
Elastomers used were Natural rubber CV 60, Ethylene Propylene Diene Monomer (EPDM, ENB, 5%,
50ML (1+4)100°C, and Chloroprene rubber (CR(W type), 50ML (1+4)100°C). The organic filler RHA was obtained from Astra chemicals Chennai (white rice husk ash) and Kothari bio fuels Ltd (black rice husk ash), Chennai. Other additives such as FEF, SRF and HAF carbon blacks, ZnO (zinc oxide), stearic acid, TMQ (2,2,4-Trimethyl-1,2-dihydroquinoline), aromatic oil, paraffinic oil, CBS (n-cyclohexyl-2 benzothiazolesulphenamide), TMTD (tertra methyl thiuram disulphide), sulphur, MgO (magnesium oxide), ETU(ethylene thiourea) were of standard chemicals used in rubber science laboratory.

3.2 Preparation of Rubber Compounds

All compounds were prepared in a 1 liter lab size kneader (SMM-LAB-1L-5HP, Santosh, India) and two roll mill. The rubber along with the activators, reinforcing fillers and process oil was mixed thoroughly in the kneader of size 1 liter for about 25 min. The final batch was obtained by mixing the masterbatch with accelerators and activators in water cooled two roll mill, 6”×13”(SMX-LAB-613, Santosh-GC), operating at friction ratio of 1.4:1, as per ASTM D3182.

Table 3: Formulation for NR CV 60 (control and test mixes containing rice husk ash as indicated)

| Ingredients                     | Phr |
|---------------------------------|-----|
| Natural rubber CV 60            | 100 |
| TMQ\(^1\)                      | 1.5 |
| ZnO\(^2\)                      | 3.0 |
| Stearic Acid\(^2\)              | 1.5 |
| HAF carbon black\(^3\)         | 30  |
| RHA (black/white)               | 0,10,20,30 |
| Aromatic Oil\(^4\)              | 5.0 |
| CBS\(^5\)                      | 1.5 |
| Sulphur\(^6\)                  | 1.5 |

\(^1\)High Abrasion Furnace grade carbon black;
\(^2\)Activator for diene rubber in sulphur crosslinks;
\(^3\)Activator in combination with ZnO (reaction product formed in situ);
\(^4\)Toaid in fine carbon black incorporation;
\(^5\)Delayed accelerator in sulphur crosslinks;
\(^6\)Elemental sulphur for creating sulphur bridges in rubber for every 100-400 repeating unit.
Table 4: Formulation for EPDM control as well as Rice Husk Ash compounds

| Ingredients                     | Phr |
|---------------------------------|-----|
| EPDM                            | 100 |
| FEF\(^a\)                      | 50  |
| RHA(white/black)                | 0,10,20,30 |
| Paraffinic Oil\(^b\)            | 30  |
| ZnO                             | 3   |
| Stearic Acid                    | 2   |
| CBS                             | 1.5 |
| TMTD\(^c\)                      | 1.5 |
| Sulphur                         | 1.5 |

\(^a\) Fast Extrusion Furnace grade carbon black; 
\(^b\) Is compatible with EPDM; 
\(^c\) TMTD is used in EPDM as secondary accelerator to boost the reactivity of CBS.

Table 5: Formulation for Polychloroprene rubber control as well as RHA filled compounds

| Ingredients                     | Phr |
|---------------------------------|-----|
| Poly chloroprene rubber         | 100 |
| FEF                             | 15  |
| SRF                             | 15  |
| RHA(white/black)                | 0,10,20,30 |
| Stearic acid                    | 2   |
| MgO\(^a\)                       | 4   |
| ZnO\(^b\)                       | 5   |
| ETU\(^c\)                       | 1   |

\(^a\) Cure activator in metal oxide cure of polychloroprene rubber; 
\(^b\) Cross linkingagent; 
\(^c\) Ethylenethiourea, organic accelerator.

3.3 Mooney Scorch Tests

The scorch test was done on the compound at temperatures 135°C and 145°C for white rice husk ash compounds. While black rice husk ash compounds were tested at 125°C, 135°C and 145°C. The tests were carried out using Ektron Mooney viscometer. The Mooney scorch traces are given in Figs. 4 to 18.
With the test results it can be inferred that the WRHA is interfering the sulfur cross linking in NR.
In sulphur cured EPDM compounds particularly the compound containing 20 phr of white rice husk ash, the onset of incipient cross linking is noticed to be faster, whereas 30 phr and 10 phr additions did not present such trend.
In natural rubber and chloroprene compounds increased addition of white rice husk ash has proved to be scorcher than the respective control compounds. In chloroprene compounds, the viscosity increase is more pronounced.

The presence of white rice husk ash (silica rich) has altered the cure time at all test temperatures. The effect in cure time is not due to increase in viscosity alone even though there is a marginal increase in the minimum viscosity with the WRHA loading.

**Figure 10:** NR CV 60 with BRHA at 125°C

**Figure 11:** NR CV 60 with BRHA at 135°C
Figure 12: NR CV 60 with BRHA at 145°C

Figure 13: EPDM with BRHA at 125°C

Figure 14: EPDM with BRHA at 135°C
Figure 15: EPDM with BRHA at 145°C

Figure 16: Chloroprene rubber with BRHA at 125°C
The black rice husk ash affects the physical chemistry of rubber system regardless of the functionality of the repeating units and the cross linking mechanism. The minimum viscosities increase in all compounds and the scorching rates also increase.

4 Results and Discussion

4.1 Hardness

The hardness tests were conducted on all 21 samples prepared using shore-A durometer. The various white rice husk ash and black rice husk ash compounds were compared and studied with the control compounds. The tests were conducted at room temperature.

Table 6: Durometer hardness comparison of NR vulcanisates

| Samples               | Shore A hardness |
|-----------------------|------------------|
| NR control            | 53               |
| NR 10 WRHA +30 HAF    | 56               |
The samples were prepared using compression molding machine with button mould at temperature 170°C under pressure of 100 bar (1500 psi) for 15 minutes. Here both the compounds increased in hardness with RHA filler addition; the WRHA filled compounds’ hardness was high compared to BRHA vulcanisates.

| Samples                     | Shore A hardness |
|-----------------------------|------------------|
| NR 20 WRHA +30 HAF          | 59               |
| NR 30 WRHA +30 HAF          | 62               |
| NR 10 BRHA +30 HAF          | 54               |
| NR 20 BRHA +30 HAF          | 57               |
| NR 30 BRHA +30 HAF          | 59               |

**Table 7:** Shore A hardness comparison of EPDM compounds

EPDM with RHA vulcanizates irrespective of the dosage and the type, show hardness around 50. This is also sulphur cured like NR. The steady resistance to surface indentation shows that the effect of RHA is dependent on the extent of physical entanglement which is almost absent in EPDM.

| Samples                     | Shore A hardness |
|-----------------------------|------------------|
| Control (0 RHA + 50 FEF)    | 49               |
| EPDM 10 WRHA + 50 FEF       | 46               |
| EPDM 20 WRHA + 50 FEF       | 52               |
| EPDM 30 WRHA + 50 FEF       | 55               |
| EPDM 10 BRHA + 50 FEF       | 47               |
| EPDM 20 BRHA + 50 FEF       | 48               |
| EPDM 30 BRHA + 50 FEF       | 50               |

**Table 8:** Comparison of Shore A hardness of CR compounds

In chloroprene rubber, which is known for crystallinity and structural integrity is largely derived from the entanglement, the resistance to surface indentation increases pronouncedly. The black rice husk ash interacts with the rubber to a larger extent.

**4.2 Rebound Resilience Test**

Rebound resilience test were done using vertical rebound tester with button samples prepared.
Table 9: Rebound Resilience of NR CV 60 compounds

| Sample                      | Rebound resilience |
|-----------------------------|--------------------|
| NR control                  | 56                 |
| NR 10 WRHA 30 Black         | 55                 |
| NR 20 WRHA 30 Black         | 53                 |
| NR 30 WRHA 30 Black         | 51                 |
| NR 10 BRHA 30 Black         | 56                 |
| NR 20 BRHA 30 Black         | 53                 |
| NR 30 BRHA 30 Black         | 48                 |

The resilience is low for NR of 50 Shore A. It means that the rice husk ash holds the cross linked network tightly onto the surface. It also means that the vulcanizates may serve as effective vibration dampers.

EPDM vulcanizates as expected (from their hardness values) possess more rubberiness with higher resilience. This trend is seen in all cases and in case of black rice husk ash the trend is more pronounced.

The loss of rubberiness is prominent among CR vulcanizates.

Table 10: Rebound Resilience of EPDM with RHA composites

| Samples                     | Rebound Resilience (%) |
|-----------------------------|------------------------|
| EPDM control                | 56                     |
| EPDM 10 WRHA 50 Black       | 57                     |
| EPDM 20 WRHA 50 Black       | 54                     |
| EPDM 30 WRHA 50 Black       | 57                     |
| EPDM 10 BRHA 50 Black       | 63                     |
| EPDM 20 BRHA 50 Black       | 58                     |
| EPDM 30 BRHA 50 Black       | 62                     |

Table 11: Rebound Resilience of CR with RHA composites

| Sample                      | Rebound Resilience |
|-----------------------------|--------------------|
| CR control                  | 51                 |
| CR 10 WRHA 30 Black         | 48                 |
| CR 20 WRHA 30 Black         | 45                 |
| CR 30 WRHA 30 Black         | 43                 |
| CR 10 BRHA 30 Black         | 46                 |
| CR 20 BRHA 30 Black         | 41                 |
| CR 30 BRHA 30 Black         | 37                 |
The black rice husk ash with its needle like carbon black composition holds the rubber segments tightly on the surface and restricting them from being resilient. This observation is elucidated with the morphology of fracture surfaces and the results are presented subsequently.

4.3 Mechanical Properties

The objective of the investigation is to understand the role of RHA as reinforcing filler to replace carbon black and silica. Considering the implication of tensile and tear properties, this section deals with these experimental values. The standard specimens were uniformly tested with the rate of elongation at 500 mm/min at room temperature. The surface features of failed samples are discussed concurrently.

The 10BRHA compound of NR had better tensile properties as well as high elongation. The SEM fractography (Fig. 21) shows that the BRHA was incorporated homogenously and thus resulting in better tensile but due to the micro level impurities like unburnt husk fibers the compound would have failed at that point, were the tensile fracture has occurred.

| Sample          | Thickness, mm | Tensile strength (MPa) | elongation at break (%) |
|-----------------|---------------|------------------------|-------------------------|
| NR control      | 1.90          | 25.5                   | 693                     |
| NR 10 WRHA      | 1.88          | 18.70                  | 530                     |
| NR 20 WRHA      | 1.91          | 18.13                  | 536                     |
| NR 30 WRHA      | 1.91          | 20.15                  | 544                     |
| NR 10 BRHA      | 1.78          | 19.85                  | 683                     |
| NR 20 BRHA      | 1.80          | 16.21                  | 668                     |
| NR 30 BRHA      | 1.81          | 15.11                  | 643                     |

Figure 19: Tensile properties of NR CV 60 compounds
Figure 20: Tear properties of NR CV 60 compounds

Figure 21: SEM fractography for NR CV 60 + 10 phr BRHA compound

Figure 22: SEM fractography for NR with 30phr BRHA composite
In the above fractography there is a depiction of flow lines in the cured compound which has weakened the elastomer itself. The presence of flow lines was a result of increased addition of BRHA. Certain portion indeed depict that the tensile elongation was good since it had micro elongations that could be seen in the above SEM image.

Comparing the corresponding tensile properties and elongation at break, it is easily depicted that the white rice husk ash compounds had medium elongation with better tensile strength, whereas the compound containing black rice husk ash showed too much of elongation similar that to the control compound but with increased BRHA addition the properties began to reduce to around 15.0 MPa. While with WRHA compound, increased addition of filler resulted in better properties but not equal to the control compound around 20.0 MPa for 30 Phr WRHA added NR vulcanisate. The incorporation of rice husk ash has lowered the tear properties. The control had 8.07 kN/m, but increased RHA filler addition in particular the BRHA has impaired the tear properties heavily.

![Figure 23: Tensile properties of EPDM with WRHA and BRHA](image1)

![Figure 24: SEM fractography of EPDM with 10phr BRHA](image2)
The above SEM image is of tear fractured vulcanisate of EPDM+10BRHA. Here the fracture occurred evenly and there is a depiction of flowlines. In case of NR, the flow lines were noticed in 30 phr loading; in EPDM it is noticed in loading of 10 phr of rich husk ash.

The SEM fractography of EPDM 30 BRHA (Fig. 25) is much different as compared with other compounds, where it had many micro level elongations and tensile failure and certain places remain intact. This may be due to filler agglomeration in certain areas thus giving good properties but at the same time not being present in other areas. These vulcanisates indeed had good elongation at break around 500%.

**Table 13: Tear Properties of NR CV 60 compound**

| Sample          | Load (Kgf) | Tear strength (kN/m) |
|-----------------|------------|----------------------|
| NR control      | 15.34      | 8.07                 |
| NR 10 WRHA      | 10.39      | 5.44                 |
| NR 20 WRHA      | 6.80       | 3.94                 |
| NR 30 WRHA      | 7.64       | 3.87                 |
| NR 10 BRHA      | 6.72       | 3.77                 |
| NR 20 BRHA      | 5.25       | 2.91                 |
| NR 30 BRHA      | 4.07       | 2.25                 |

**Table 14: Tensile properties of EPDM compounds**

| Sample          | Thickness, mm | Tensile strength (MPa) | Elongation at break (%) |
|-----------------|---------------|------------------------|-------------------------|
| EPDM control    | 1.88          | 6.97                   | 383                     |
| EPDM +10 WRHA   | 1.90          | 6.73                   | 317                     |
| EPDM +20 WRHA   | 1.91          | 7.81                   | 407                     |
| EPDM +30 WRHA   | 1.90          | 8.32                   | 401                     |
| EPDM +10 BRHA   | 1.79          | 7.41                   | 433                     |
| EPDM +20 BRHA   | 1.80          | 7.81                   | 420                     |
| EPDM +30 BRHA   | 1.78          | 7.03                   | 493                     |

Unlike BRHA+EPDM composites, the presence of silica (white husk ash, Fig. 26) there were no flow lines and tensile fracture has occurred all over the compound. The 20 phr WRHA compound had tensile of 7.8MPa and poor elongation of 300% unlike BRHA compounds which had good elongation.

These test results depict a clear picture that compared to NR vulcanisates they do present different patterns. RHA filler (BRHA and WRHA) at 20 phr of addition in the compound has tensile strength of 7.8 MPa. And 30 phr of WRHA compound had 8.0 MPa of tensile strength. Increased filler addition of BRHA reduced the properties.
Figure 25: SEM fractography of EPDM with 30 phr BRHA

Figure 26: SEM fractography of EPDM 20 + WRHA

Table 15: Tear properties of EPDM vulcanisates

| Samples            | Load (Kgf) | Tear strength (kN/m) |
|--------------------|------------|----------------------|
| EPDM control       | 2.13       | 1.183                |
| EPDM 10 WRHA       | 4.08       | 2.158                |
| EPDM 20 WRHA       | 3.79       | 2.03                 |
| EPDM 30 WRHA       | 3.83       | 2.015                |
| EPDM 10 BRHA       | 2.69       | 1.502                |
| EPDM 20 BRHA       | 3.99       | 2.22                 |
| EPDM 30 BRHA       | 2.58       | 1.44                 |
Comparing the elongation at break, increased addition of RHA increased the strain at break. That too in BRHA at 30 phr the strain was high around 500%.

**Table 16:** Tensile property comparison of CR compounds

| Sample       | Thickness (mm) | Tensile strength (MPa) | Elongation at break (%) |
|--------------|----------------|------------------------|-------------------------|
| CR control   | 2.10           | 16.02                  | 334                     |
| CR 10 RHA    | 2.11           | 13.92                  | 331                     |
| CR 20 RHA    | 2.09           | 13.13                  | 326                     |
| CR 30 RHA    | 2.11           | 12.6                   | 273                     |
| CR 10 BRHA   | 2.11           | 13.25                  | 244                     |
| CR 20 BRHA   | 2.23           | 14.68                  | 231                     |
| CR 30 BRHA   | 2.37           | 13.38                  | 319                     |

**Figure 27:** Tensile property of CR with WRHA and BRHA

**Figure 28:** SEM fractography of CR+ 10 WRHA
Figure 29: SEM fractography of CR 20 RHA

This SEM fractography presents some interesting interpretations in contrast to the NR and EPDM counterparts. The flow lines occur in minimum addition of white rice husk ash. Previously the flow lines were observed in black rice husk ash compounds for both NR and EPDM composites. Scorch tests with CR compounds also depicted a picture that addition of RHA made the compound scorcher. The tensile strength of CR+10 WRHA was 13.9 MPa, with a strain at break of 330%.

These SEM images show flowlines that have occurred incurred composites with tensile strength of 13.0 MPa and an elongation of 330% at break.

Here the addition of BRHA has increased the flow lines. These flow lines make the cured rubber compound weak and to experience low elongation and brittle failure in tension mode. CR vulcanisate containing 20 BRHA showed brittle failure with an elongation of 230% at break. For technical application of rubber, a certain level of elongation is critical.

Figure 30: SEM fractography of CR + 20 BRHA
Table 17: Tear strength of CR+ RHA vulcanizates

| Sample      | Load (Kgf) | Tear strength (kN/m) |
|-------------|------------|----------------------|
| CR control  | 7.07       | 3.35                 |
| CR 10 WRHA  | 5.87       | 2.73                 |
| CR 20 WRHA  | 4.81       | 2.29                 |
| CR 30 WRHA  | 4.68       | 2.25                 |
| CR 10 BRHA  | 5.77       | 2.65                 |
| CR 20 BRHA  | 4.53       | 2.15                 |
| CR 30 BRHA  | 5.17       | 2.40                 |

The tear properties were similar to that of EPDM and NR composites. The tear strength remains largely unaffected with RHA addition with gradual decrease in higher loading of RHA.

5 Conclusion

The use of Rice Husk Ash (RHA) as filler caused different results in different rubbers. It increased 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. In NR and EPDM composites were vulcanised with sulphur cross linking. The difference among NR and EPDM may be attributed to the intervention of the RHA with the strain induced crystallization of NR.

The increased addition of RHA showed decrease in properties especially in chloroprene composites. At the same time, it produced scorcher compounds, which may be due to certain chemical reaction between the cross linking of rubber and the impurity (for examples, metal oxides) present in the RHA. Further studies could be carried out to optimize the properties in the future.

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