Use of Rice Husk and Phenols Extracted from it as Filler and Antioxidant Respectively in Vulcanization Studies of NR

A.P. Kuriakose* and G. Rajendran**
Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology
Cochin-682 022, India

Received 15 August 1998; accepted 29 November 1999

ABSTRACT

In the present study, the rice husk is used as filler in natural rubber (NR) to observe its reinforcing effect on the rubber vulcanization. The effect of variation of particle size and of filler loading is investigated. The results of the study indicated that much reinforcement is not obtained by the incorporation of husk in different formulations. When used in smaller particle size, however, some reinforcement effect is noticed. This effect can further be increased by incorporation of resorcinol and hexamine in the compound recipe. In the next part of the study, the mixture of phenols consisting of ferulic, vanillic, p-coumaric, sinapic p-hydroxy benzoic, salicylic and indoleacetic acid extracted from rice husk has been tried as antioxidant in NR gum and filled vulcanizates. The results obtained were compared with those of control mixes containing styrenated phenol. The cure characteristics and vulcanizate properties were evaluated. The results indicated that there is not much variation in cure characteristics or tensile properties between control and experimental sets. Further, the antioxidant protection given by phenols from rice husk is comparable with that of styrenated phenol.

Key Words: rice husk, phenol, filler, antioxidant, natural rubber

INTRODUCTION

In India, about 20 million tonnes of rice husk is obtained as by-product in the rice milling industry. It forms 16–25% by weight of the paddy. It is used as a fuel in husk fired furnaces to produce hot air for drying parboiled paddy and also for generating steam for parboiling process [1]. It can be used for preparing chemicals like silicon carbide, silicon tetrachloride, [2, 3] acetic acid, propionic acid, phenol and cresol.

The major chemical components of rice husk are cellulose lignin, silica and pentosan and minor components are fat, protein and phenols [4]. The free phenols present in rice husk range from 77 to 390...
µg/g depending upon the life of the rice seed and its storage period [5, 6]. The methanol extract of wild rice hulls showed antioxidative activity when added to beef mince [7]. Though there are reports on the extraction of phenols from husk, there is no mention however in the literature on the use of these phenols in the polymer industry. There is also no report on systematic study on the use of rice husk as filler in rubber even though many other short fibres were tried in rubber compounding [8, 9].

In rubber industry, the fillers are classified into reinforcing and inert types and that of antioxidants are classified into two groups viz. amines and phenols. Amines are referred to as staining antioxidants as they tend to discolor non-black vulcanizates on exposure to light. The phenols generally used are the substituted types and they are non-staining in nature. The resulting protection is always more apparent in natural rubber (NR) than in synthetic rubbers partly because of the inherent ageing stability and also because of the stabilizer added during the manufacture of these rubbers.

The antioxidants used for rubber compounding at present especially the amine types are somewhat toxic in nature, whereas, the antioxidant extracted from rice husk is non-toxic.

In this study, the rice husk was used as such and also at different mesh sizes and at different filler loadings as filler in NR. Cumarone indene resin and resorcinol with hexamine were also tried along with husk in some of the mixes. The mixture of phenols extracted from rice husk was tried as antioxidant in NR gum and NR filled compounds and it was compared with control. All the mixes were evaluated for the cure characteristics and the vulcanizates were tested for the different tensile properties. It is also noticed that the rice husk does not have any adverse effect on processing or curing characteristics of the mixes.

**EXPERIMENTAL**

The elastomer used in the present study is NR (ISNR-5). Activator: zinc oxide; accelerators: MBTS, TMTD; co-activator: stearic acid; fillers: carbon black, precipitated silica; processing oils: aromatic oil, naphthenic oil and diethylene glycol, and silane coupling agent, sulphur and styrenated phenol used are all of rubber grade [10]. Chloroform, methanol, n-hexane, Cl resin, hexamethylene tetramine and resorcinol are of analytical grade. Rice husk was used as such and also after pulverizing and sieving into different mesh sizes.

**Extraction of Phenols from Husk**

Soxhlet extraction apparatus was used for extracting oil and phenols from husk. Husk (2 kg) from CR 1009 rice variety was cleaned, pulverized and sieved through a 50-mesh sieve. The sieved husk of 25 g was wrapped in filter paper and placed in the tube of the extractor, which was then connected with the condenser. A plug of cotton was placed on the top of the thimble to prevent the pulverized samples from floating out as the solvent rises and being carried into the flask during the siphoning.

The sample was first extracted with n-hexane to remove the oil from the husk. Then the sample was further extracted with 1:1 mixture of chloroform and methanol [11]. The heating was controlled in such a way that the solvent siphoned over about 5 to 6 times an hour.

After the extraction was completed, the solvent was distilled off. The residue was dissolved in minimum quantity of methanol, filtered through a filter paper (Whatman No. 40, qualitative). Methanol was removed and then dried at 80°C (yield 1%).

The conventional system of rubber Vulcanization was followed in the study. The mixes were prepared on a laboratory size two roll mixing mill (30x15 cm) at a friction ratio of 1:1.25 according to the procedure given in ASTM D3285-88. The cure characteristics of the various mixes containing husk of different particle sizes were evaluated at 150°C using a Goettfert elastograph (model No. 67.85) as per ASTM D 1646 (1981). The cure rate index was determined from the cure curves of the respective mixes as 100/t90-t10, where t90 and t10 are times corresponding to the optimum cure and 10% of the vulcanization, respectively. Induction time (t8) is the time taken for one unit (0.1 NM) rise above the
minimum torque (about 5% vulcanization), optimum cure time ($t_{60}$) is the time taken for attaining 90% of the maximum torque. Elastographic scorch is calculated as the time for 10% of vulcanization.

The test specimens for determining the physical properties were prepared in standard moulds by compression moulding on a single day light, electrically heated press having 30x30 cm platens at a pressure of 11.764 MPa on the mould. The rubber compounds were Vulcanized to their respective optimum cure at 150 °C. Moulds were cooled quickly in water at the end of the curing cycle and stored in a cool, and dark place for 24 h and were used for subsequent physical tests.

Tensile properties of the vulcanizates were determined as per ASTM D 412 (1980) using dumbbell specimens on a Zwick Universal Testing Machine (Model 1445). Tear resistance was determined as per ASTM D 624 (1981) using un nicked, 90 ° angle test pieces. The hardness (shore A) of the moulded samples was determined using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1981).

Compression set for vulcanized samples was determined as per ASTM D 395-89 (method B). The abrasion resistance of the samples was determined using a DIN abrader (DIN 53515). Sample having a diameter of 6±0.2 mm and thickness of 6 mm was kept on a rotating sample holder and a 10 N load was applied. Abrasion loss is expressed as the volume of the test piece abraded by its travel through 42 m on standard abrasive surface.

Dunlop tripsometer was used to measure rebound resilience and it was calculated from the initial and rebound angles. Ageing studies were carried out according to ASTM D 537-88. Dumb bell samples were kept in an air oven at 100 °C for 24 h. Physical properties like tensile strength, elongation-at-break, modulus etc., were measured after ageing.

Knowing the values of these tests before ageing, the retention of these properties was calculated for assessing the effect of ageing.

The concentration of cross-links (cross-link density) of the vulcanizates was determined from the equilibrium swelling data as per the procedure reported by us earlier [12].

RESULTS AND DISCUSSION

Rice husk was used as such and also at different mesh sizes, viz. 50, 100 and 200 and at different filler loadings like 25, 50 and 100 phr in this study. The different formulations used in these experiments are given in Table 1. Cumarone indene resin and resorcinol with hexamine were also tried along with husk in some of the mixes. The mixture of phenols extracted from rice husk was examined as antioxidant in NR gum, NR-carbon black and NR-silica filled systems using the formulations given in Table 2. The control mixes containing styrenated phenol were also prepared and their properties compared with those of the mixes containing antioxidant from husk.

The cure curves of the mixes containing 25, 50 and 100 phr of rice husk as such as filler are given in Figure 1. Similarly the cure curves of those mixes containing rice husk of 50, 100 and 200 meshes at 25, 50 and 100 phr levels of loading are given in Figure 2. The different cure characteristics of the mixes evaluated are given in Table 3. From the result it is clear that the torque developed is minimum for the mixes containing 25 phr of rice husk and is maximum for the mixes containing 100 phr of rice husk. Slightly higher torque and a slight reduction in optimum cure time are observed when the husk used is of smaller particle size. Cure curves of the mixes containing 50 phr rice husk of 100 mesh with cumarone indene resin (CI resin) and with resorcinol and hexamine are given in Figure 3. The CI resin is seen to have no influence on
Table 1. Formulation of mixes containing husk as such and at different particle sizes.

<table>
<thead>
<tr>
<th>Mix</th>
<th>IA</th>
<th>IB</th>
<th>IC</th>
<th>II A</th>
<th>II B</th>
<th>II C</th>
<th>III A</th>
<th>III B</th>
<th>I VA</th>
<th>I VB</th>
<th>I VC</th>
<th>VA</th>
<th>VB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Styrenated phenols</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Mercapto benzothiazyl disulphide</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Tetramethyl thiuram disulphide</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Husk (as such)</td>
<td>25</td>
<td>50</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Husk (50 mesh)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>25</td>
<td>50</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Husk (100 mesh)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>25</td>
<td>50</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Husk (200 mesh)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>25</td>
<td>50</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Husk (100 mesh) with Cl resin</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Husk (100 mesh) with resorcinol and hexamine</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>2.5</td>
<td>5.0</td>
<td>10.0</td>
<td>2.5</td>
<td>5.0</td>
<td>10.0</td>
<td>2.5</td>
<td>5.0</td>
<td>10.0</td>
<td>2.5</td>
<td>5.0</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

As far as induction time and scorch time are concerned, they were 3.5 and 4.3 min, respectively for the mixes containing 25, 50 and 100 phr of husk as filler, whereas, it was in the range of 3.1 to 3.4 min for the other mixes containing 25, 50 and 100 phr of husk of different particle sizes. Optimum cure time was 7.2 to 7.5 min for the former mixes whereas it was in the range of 7.0 to 7.4 min for the latter set of experiments. The induction time for the mixes containing husk with Cl resin and with resorcinol and hexamine was 3.3 and 2.1 min, respectively. The scorch time for above mixes was 4.2 and 2.5 min while optimum cure time was 7.2 and 8.4 min, respectively.

The cure curves of NR gum compounds containing phenols from rice husk and those containing styrenated phenol (control) are given in Figure 4.
compounds containing phenols from rice husk and those containing styrenated phenol are also in the same pattern of gum compounds. Optimum cure time, cure rate index and scorch characteristics are given in Table 4. From the cure curves, it can be seen that the torque developed was maximum in mixes containing antioxidant from husk. There was not much variation in the induction time, scorch time, optimum cure time among the different mixes. It is evident that the addition of phenolic antioxidant from husk does not have any adverse effect on the cure characteristics of different mixes under review. The different cure values obtained are comparable to those obtained from control mixes.

Cross-link Density
The cross-link density values of the compounds containing antioxidant from husk and those with styrenated phenol are given in Table 5. From the results, it is seen that the cross-link density value is highest for carbon black filled compounds followed by silica filled and then unfilled vulcanizates. A slightly higher cross-link density is noticed for the mixes containing antioxidant from husk compared to the control mixes. But this difference is only marginal among the mixes of NR gum, NR-carbon black and NR-silica. These differences in cross-link density values are also reflected in the results of physical properties reported in this section.

Table 2. Use of phenols obtained from husk as antioxidant in filled and unfilled vulcanizates of NR.

<table>
<thead>
<tr>
<th>Mix</th>
<th>VIA</th>
<th>VIB</th>
<th>VIIA</th>
<th>VIIB</th>
<th>VIIIa</th>
<th>VIIIb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Mercaptobenzothiazyl disulphide</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Tetramethyl thiuram disulphide</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Styrenated phenol (control)</td>
<td>1.0</td>
<td>-</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Phenols from husk</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Carbon black (HAF 330)</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Precipitated silica (vulkasil)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Naphthenic oil</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Silane coupling agent</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 3. Cure characteristics of mixes containing husk of different particle sizes (cured at 150°C).

<table>
<thead>
<tr>
<th>Cure characteristics</th>
<th>IA</th>
<th>IB</th>
<th>IC</th>
<th>IIa</th>
<th>IIb</th>
<th>IIc</th>
<th>IIIa</th>
<th>IIIb</th>
<th>IIIc</th>
<th>IVA</th>
<th>IVB</th>
<th>IVC</th>
<th>VA</th>
<th>VB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimum cure time t&lt;sub&gt;0&lt;/sub&gt; (min)</td>
<td>7.2</td>
<td>7.4</td>
<td>7.5</td>
<td>7.1</td>
<td>7.3</td>
<td>7.4</td>
<td>7.0</td>
<td>7.2</td>
<td>7.3</td>
<td>7.0</td>
<td>7.1</td>
<td>7.2</td>
<td>7.2</td>
<td>8.4</td>
</tr>
<tr>
<td>Elastographic scorch time t&lt;sub&gt;0&lt;/sub&gt; (min)</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
<td>4.2</td>
<td>4.2</td>
<td>4.2</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Cure rate index</td>
<td>34.48</td>
<td>32.25</td>
<td>31.25</td>
<td>34.48</td>
<td>32.25</td>
<td>31.25</td>
<td>34.48</td>
<td>32.25</td>
<td>31.25</td>
<td>33.33</td>
<td>32.26</td>
<td>31.25</td>
<td>33.33</td>
<td>16.94</td>
</tr>
<tr>
<td>Induction time (min)</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>3.4</td>
<td>3.4</td>
<td>3.4</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.3</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Use of Rice Husk and Phenols Extracted from it as Filler and Antioxidant

Tensile and Other Physical Properties
The tensile properties of the vulcanizates containing husk as filler are given in Table 6. As expected, it is seen that the vulcanizates having finer particles of husk has shown better tensile strength compared to the vulcanizates containing coarse particles of husk at the same filler loading. In the case of 25 phr filler loading, the vulcanizates containing husk of 200 mesh size have given the tensile strength value of 16.44 MPa, whereas, in the case of other vulcanizates containing husk of 100 mesh size, 50 mesh size and unsieved husk have given the tensile strength values of 16.16, 9.53 and 6.69 MPa, respectively. Elongation-at-break is a maximum for the vulcanizates containing 25 phr filler loading and minimum for the vulcanizates containing 100 phr. The elongation value is also a maximum for the vulcanizates containing coarse particles of husk at the same filler loading.

The same trend is observed in the case of modulus value as well. The modulus value generally increases as the quantity of husk used increases. The results obtained for the mixes containing Cl resin and resorcinol with hexamine are also given in Table 6. Resorcinol with hexamine and Cl resin are known to promote adhesion between rubber and filler and thereby improve tensile properties [13]. The data obtained in this study also indicate that the tensile strength of the vulcanizates increases with the incorporation of these resins.

The cumarone indene resin have better effect on tensile strength and elongation value compared to resorcinol with hexamine. Cl resin does not seem to have any influence on modulus value, whereas, resorcinol with hexamine increases the modulus with the decrease of elongation.

In the second part of the study, phenols extracted from husk was used as antioxidant in NR gum, NR-carbon black and NR-silica systems using styrenated phenol as control. The cure characteristics of various mixes are given in Table 4 and it was explained earlier. The tensile and other physical properties obtained for these various mixes are given in Table 6. From the table it is clear that in the case of gum formulations, the initial tensile strength and modulus value for the mix containing styrenated phenol are higher compared to the mix containing phenolic antioxidant from husk. The initial tensile strength was more or less the same for both the mixes containing carbon black (i.e., the mixes containing antioxidant from husk/styrenated phenol).

In the case of carbon black filled system, the modulus value was higher for the control compared to experimental set. The tensile properties of the samples after ageing are also given in Table 5. Regarding the after ageing properties, the retention of tensile properties was better for the mix containing antioxidant from husk compared to the reference mix in NR gum.

Table 4. Cure characteristics of mixes containing phenolic antioxidants from husk.

<table>
<thead>
<tr>
<th>Cure characteristics</th>
<th>Mix No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VIA</td>
</tr>
<tr>
<td>Optimum cure time t90 (min)</td>
<td>6.2</td>
</tr>
<tr>
<td>Elastographic scorch time t10 (min)</td>
<td>3.5</td>
</tr>
<tr>
<td>Cure rate index</td>
<td>37.03</td>
</tr>
<tr>
<td>Induction time (min)</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Table 5. Physical properties of the vulcanizates containing phenolic antioxidant from husk and styrenated phenol.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mix number</th>
<th>Parameter</th>
<th>Mix number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VIA</td>
<td>VIB</td>
<td>VIA</td>
</tr>
<tr>
<td></td>
<td>(1) (2) (3) (4)</td>
<td>(5) (6) (7)</td>
<td>(8) (9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>23.01 22.94</td>
<td>26.88 26.58 24.65 24.68</td>
<td>13.51 14.30</td>
</tr>
<tr>
<td></td>
<td>AA</td>
<td></td>
<td>19.63 19.67 19.30 20.16</td>
</tr>
<tr>
<td>Elongation-at-break (%)</td>
<td>728 730</td>
<td>382 425 576 585 392 365</td>
<td>557 574 337 337 392 365</td>
</tr>
<tr>
<td></td>
<td>AA</td>
<td></td>
<td>557 574 337 337 392 365</td>
</tr>
<tr>
<td>Modulus at 200 % elongation (MPa)</td>
<td>2.24 1.93</td>
<td>8.78 8.55 4.35 4.35</td>
<td>1.93 1.61</td>
</tr>
<tr>
<td></td>
<td>34 35</td>
<td>127 129 74 75</td>
<td>35 1.61</td>
</tr>
<tr>
<td>Tear strength (N/mm)</td>
<td>30.34 29.98</td>
<td>36.47 36.55 50.00 50.00</td>
<td>29.98 1.61</td>
</tr>
<tr>
<td>Compression set (%)</td>
<td>40 40</td>
<td>65 65 87 67</td>
<td>40 1.61</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>7.066 7.066</td>
<td>5.217 5.186 5.165 5.139</td>
<td>7.066 1.61</td>
</tr>
<tr>
<td>Abrasion loss (cm³/h)</td>
<td>76.12 76.54</td>
<td>54.11 54.11 54.43 54.43</td>
<td>76.54 1.61</td>
</tr>
<tr>
<td>Resilience (%)</td>
<td>40.46 40.46</td>
<td>74.00 74.12 66.85 66.92</td>
<td>40.46 1.61</td>
</tr>
<tr>
<td>Cross-link density (mmol/kg)</td>
<td>40.46 40.46</td>
<td>74.00 74.12 66.85 66.92</td>
<td>40.46 1.61</td>
</tr>
</tbody>
</table>

In the case of carbon black filled systems, the initial tensile strength was better for the reference mix compared to the mix containing antioxidant from husk. As expected, a reverse trend was noticed for elongation values. The retention of tensile strength on heat ageing was better for the mix containing antioxidant from husk. Almost the same trend in initial tensile strength, elongation-at-break and after ageing properties is noticed for silica filled compounds also.

The results are indicative of the fact that the phenols extracted from rice husk shows a strong antioxidant character in NR gum, NR carbon black and NR-silica systems. Some of the other physical compounds.

Table 6. Tensile properties of the vulcanizates containing husk as such and at different mesh size as filler.

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>Filler loading of husk (phr)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation-at-break (%)</th>
<th>Modulus at 200 % elongation (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IA</td>
<td>25</td>
<td>6.69</td>
<td>543</td>
<td>1.61</td>
</tr>
<tr>
<td>IB</td>
<td>50</td>
<td>3.20</td>
<td>381</td>
<td>1.58</td>
</tr>
<tr>
<td>IC</td>
<td>100</td>
<td>1.74</td>
<td>223</td>
<td>1.82</td>
</tr>
<tr>
<td>IIA</td>
<td>25</td>
<td>9.53</td>
<td>601</td>
<td>1.88</td>
</tr>
<tr>
<td>IIB</td>
<td>50</td>
<td>6.40</td>
<td>541</td>
<td>1.87</td>
</tr>
<tr>
<td>IIC</td>
<td>100</td>
<td>3.20</td>
<td>319</td>
<td>1.90</td>
</tr>
<tr>
<td>IIIA</td>
<td>25</td>
<td>16.16</td>
<td>634</td>
<td>2.77</td>
</tr>
<tr>
<td>IIIIB</td>
<td>50</td>
<td>8.73</td>
<td>475</td>
<td>3.04</td>
</tr>
<tr>
<td>IIIIC</td>
<td>100</td>
<td>5.03</td>
<td>289</td>
<td>3.52</td>
</tr>
<tr>
<td>IVA</td>
<td>25</td>
<td>16.44</td>
<td>628</td>
<td>3.26</td>
</tr>
<tr>
<td>IVB</td>
<td>50</td>
<td>11.40</td>
<td>472</td>
<td>3.53</td>
</tr>
<tr>
<td>IVC</td>
<td>100</td>
<td>5.20</td>
<td>283</td>
<td>3.66</td>
</tr>
<tr>
<td>VA</td>
<td>50</td>
<td>9.78</td>
<td>509</td>
<td>3.01</td>
</tr>
<tr>
<td>VB</td>
<td>50</td>
<td>9.30</td>
<td>315</td>
<td>3.41</td>
</tr>
</tbody>
</table>
properties of the vulcanizates evaluated are hardness, compression set; tear strength, resilience and abrasion resistance. Hardness and abrasion loss values did not show significant variation among the different mixes. Tear strength was higher for the mixes containing antioxidant from husk compared to the reference mixes in all the system.

**CONCLUSION**

Rice husk as such at different particle sizes were used as fillers in NR compounding. The effect of variation of particle size and of filler loading was investigated. It is seen that much reinforcement is not effected by incorporation of the husk as such when used in different formulations. But when these fillers are used in smaller particle size, some reinforcement effect is noticed. The reinforcement can further be increased by incorporation of resorcinol and hexamine in the mix.

The husk does not have any adverse effect on processing or curing characteristics of the mixes. It is evident that this filler can be used in NR mixes when product requires low or medium tensile strength. Being a natural product it is an advantage compared to other synthetic filler used in rubber compounding.

In the second part of the study, extracted phenols from husk are being tried as antioxidants in the vulcanization studies of NR. The results obtained in this study viz., cure characteristics and vulcanizate properties (both before and after ageing) were compared with those of control mixes containing styrenated phenol. Both gum and filled vulcanizates were investig-igated. It is seen that this phenolic mixture gives antioxidant protection to the rubber comparably to a conventional antioxidant like styrenated phenol. There is no adverse effect on cure characteristics of the various mixes evaluated. These phenols do not show any adverse effect on the tensile properties of the vulcanizates either.

**REFERENCES**