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Design and analysis of single-factor experiments: Analysis of variance of the effect of rice husk ash and commercial fillers in NR compounds

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Summary

White rice husk ash (WRHA) and black rice husk ash (BRHA) were incorporated into natural rubber (NR) using a laboratory-sized two-roll mill. A conventional vulcanization system was used for curing and physical tests of the NR vulcanized involved determining of tensile and tear resistances. For comparison purposes, precipitated silica (Zeosil-175) and carbon black (N774) were used too. Using the analysis of variance of single-factor experiments, it can be concluded that: BRHA is non-reinforcing filler and its use is limited to 20 phr; WRHA is semi-reinforcing filler and the variation of filler loading (0 up to 50 phr) causes the maximum variation upon tensile strength of NR compounds; and, that although carbon black and silica are reinforcing fillers, a real reinforcement is reached up to 20 phr for tensile strength.

Introduction

Experiments are a natural part of the engineering and scientific decision-making process and statistically based experimental design techniques are particularly useful in the engineering world for improving the performance of a manufacturing process. They also have extensive application in the development of new processes. Some typical applications of statistically designed experiments in engineering design include: evaluation and comparison of basic design configurations; evaluation of different materials; selection of design parameters so that the product will work under wide variety of field conditions; and, determination of key product design parameters that impart product performance.

The production of rice, one of the major food crops in the world, generates large amounts of wastes namely rice hulls and straw. Efforts to find an utilization to these materials have resulted mostly in a low-value or limited applications. Little advantage has been taken of the high-energy content, amorphous character of the present silica

and highly cellular structure of either the hulls or the straw [1-3]. In recent years, due to growing environmental concern and the need to conserve energy and resources, efforts have been made to burn the husks under controlled conditions and to use the resultant ash as magnesium silicide (Mg_2Si) semiconductors and higher-quality solar grade silicon [4,5].

Applications of rice husk ash (RHA) as filler in polymers have been reported by Ahmad Fuad *et al*. [6,7], who observed that the incorporation of this material into polypropylene has led to a significant increase in flexural modulus, comparable to the imparted by commercial fillers such as mica. Ismail *et al.* [8-10] reported the effect of rice husk ash as filler in epoxidized natural rubber (ENR) compounds and the effect of silane coupling agents in natural rubber (NR), also compounded with RHA. In addition, da Costa *et al.* [11-15] have been reported some investigations about RHA influence in the vulcanization kinetics and mechanical properties of NR compounds. However, in all investigations cited, statistical methods were not introduced and a real optimization of results was not reached. So, in this work, black rice husk ash (BRHA) or white rice husk ash (WRHA), in according to burning conditions, were incorporated in NR compounds and their real effects on mechanical properties were evaluated using the analysis of variance as statistical tool. Commercial fillers such as silica and carbon black were used for comparison purposes.

Experimental

Materials

Natural rubber (SMR-L) was supplied by Irwin Industrial e Comercial Ltda. Zinc oxide and stearic acid were standard reference materials. Sulfur was supplied by Vetec Química Fina Ltda (RJ), and accelerator by Bann Química Ltda (SP), Brazil. Carbon black (N774) was supplied by Copebrás while precipitated silica (Zeosil-175) by Rhodia. Diethylene glycol, reagent grade, was only used in NR compounds containing silica for to avoid the deleterious effect upon vulcanization. The compositions were prepared following the formulation presented in Table 1.

Table 1: Typical formulation

Material	Concentration (phr)
Natural rubber	100
Zinc oxide	3.5
Filler	0-50
Stearic acid	2.5
CBS[a]	0.8
Aminox[b]	2.0
Sulphur	2.5

[a]N-cyclohexyl-2-benzothiazole-2-sulphenamide; [b]Antioxidant – low temperature reaction product of diphenylamine and acetone

The ashes were supplied by EMBRAPA (Empresa Brasileira de Pesquisa Agropecuária), milled, and sieved on a 325 mesh sieve before analysis by Inductively Coupled Plasma Emission Spectroscopy. The chemical composition results are shown

in Table 2. Particle size distribution, surface area and density for the two ashes are presented in Table 3 and were determined by using a Global Lab Image (SP0550) software package, an ASAP 2010 Accelerated Surface Area and Porosimetry System (through the BET method), and a glass pycnometer, respectively. Method ASTM D1512 was followed to measure pH.

Table 2: Chemical composition of rice husk ash

Chemical composition (%)	BRHA	WRHA
CaO	0.40	0.77
MgO	0.38	0.53
Fe_2O_3	0.13	0.25
K_2O	1.22	1.05
Na_2O	0.13	0.30
Al_2O_3	0.23	0.27
MnO	0.16	0.14
TiO_2	0.01	0.01
P_2O_5	0.96	1.00
SiO_2 (silica)	74.85	97.00
Loss on ignition (LOI)	21.00	0.20

Table 3: Physical properties of rice husk ash and commercial fillers

Properties	BRHA	WRHA	Silica	Carbon black
Mean particle size (μm)	2.5	2.2	0.018	0.054
Surface area (m^2/g)	110.0	7.8	185.0	29.5
Micropore area (m^2/g)	88.2	1.8	48.3	3.7
% Micropore area	80.1	22.6	31.0	12.5
Density (g/cm^3)	1.9	2.0	2.0	1.8
pH	9.5	9.4	5.7	6.4

Preparation of mixtures, rheometry and preparation of test samples

Mixing was carried out on a two-roll mix at 70°C and 1:1.25 speed ratio, according to ASTM D3182. Rice husk ash was dried at 120°C for 24 h immediately before use. The batch mass was checked and recorded. If different from theoretical value by more than 0.5%, it was rejected. The sheeted compound was conditioned at 25 ± 2°C for 24 h in a closed container before the determination of the optimum cure time by using a TI-100 Curometer, at 150°C. For mechanical properties, vulcanizates were prepared by compression molding in an electrically heated press at 150°C and 3.0 MPa. Appropriate specimens were cut and, after conditioning for 24 h, the properties were evaluated. All properties were measured along the grain direction.

Physico-mechanical testing of the samples

Stress-strain data were determined on an Instron Universal Testing Machine, Model 101, on C-type dumbbell specimens, according to ASTM D412. Other physical-mechanical test was tear strength (ASTM D624).

Analysis of the fracture surface

Examination of the facture surface was carried out on a scanning electron microscope (SEM), model JEOL JSM-5300. The objective was to get an insight into fracture mode in an attempt to draw a picture of the matrix and filler surfaces and filler dispersion. The fractured ends of the tensile specimens were mounted on aluminum slabs and spatter coated with a thin layer of gold to avoid electrical charging during examination.

Analysis of variance

The analysis of variance was applied for evaluation of the effect of rice husk ash (BRHA and WRHA) and commercial fillers (silica and carbon black) in the NR compositions. Tensile strength was considered as a function of the filler concentration in the NR compositions and the range of filler concentration of practical interest was fixed between 0 and 50 phr. Six levels of filler concentration were investigated: 0, 10, 20, 30, 40 and 50 phr. Five test specimens at each concentration level were used in this investigation. All 30 specimens were tested in random order and the data from these experiments were organized according to Tables 4 and 5 [16,17]. The same methodology was used for analysis of tear strength.

Table 4: Typical data for a single-factor experiment

Treatment	Observations				Totals	Averages
1	Y_{11}	Y_{12}	…	Y_{1n}	$\mathbf{Y_{1.}}$	$\overline{\boldsymbol{Y}}_{1.}$
2	Y_{21}	Y_{22}	…	Y_{2n}	$\mathbf{Y_{2.}}$	$\overline{\boldsymbol{Y}}_{2.}$
...	…	…	…	…	**...**	**...**
a	Y_{a1}	Y_{a2}	…	Y_{an}	$\mathbf{Y_{a.}}$	$\overline{\boldsymbol{Y}}_{a.}$
					$\mathbf{Y_{..}}$	$\overline{\boldsymbol{Y}}_{..}$

Table 5: The analysis of variance for a single-factor experiment, fixed-effects model

Source of variation	Sum of Squares (SS)	Degrees of Freedom (DF)	Mean Square (MS)	F_o
Treatments	$SS_{Treatments}$	a-1	$MS_{Treatments}$	$MS_{Treatments} / MS_E$
Error	SS_E	a(n-1)	MS_E	
Total	SS_T	an-1		

a = number of different levels of a single factor; n = number of observations; N = number total of observations (N = a*n); if $F_o > f_{\alpha,\ a-1,\ a(n-1)}$, there is an real effect when the levels are changing

The results of tensile and tear strength were interpreted using the hypotheses:

$$H_o: \tau_1 = \tau_2 = \ldots = \tau_a = 0 \qquad \textbf{(1)}$$
$$H_1 = \tau_i \neq 0 \text{ for at least one } i$$

where, if the null hypothesis is true, changing the levels of the factor has no effect on the mean response (all *N* observations are taken from a normal distribution with mean μ and variance σ^2) and the ratio F_o has an *F*-distribution with ***a - 1*** and ***a (n - 1)***

degrees of freedom (Table 5). If $F_o > f_{\alpha,\, a-1,\, a(n-1)}$, where α is a significance level, H_o is rejected and filler concentration in the NR compositions significantly affects tensile or tear strength of the NR.

Multiple comparison methods were also applied in the cases where the analysis of variance proved that the null hypothesis should be rejected. In this case, procedures for comparing individual treatments means are adopted. *Graphical comparison of means* and *Fisher's least significant difference* methods were used [16,17].

$$SS_T = \sum_{i=1}^{a}\sum_{j=1}^{n} y_{ij}^2 - \frac{y_{..}^2}{N} \; ; SS_{Treatments} = \sum_{i=1}^{a} \frac{y_{i.}^2}{n} - \frac{y_{..}^2}{N} \; ; \; SS_E = SS_T - SS_{Treatments}$$

Results and discussion

The effect of BRHA, WRHA and commercial fillers on tensile strength of NR compounds is shown in Figure 1. For WRHA, increasing the filler content increases this property until a maximum value is reached at about 20 phr filler loading. Further increase in filler content reduces the tensile strength. As the filler loading is increased, more surface area is available for interaction between filler particles and rubber molecules; hence reinforcement increases with an increase in filler loading. However, maximum reinforcement level is eventually reached, at about 20 phr of WRHA, after which dilution effect occurs with undispersed filler agglomerates preponderate. For BRHA-filled NR vulcanizates, tensile strength is lower than NR vulcanizates containing WRHA along the entire loading range. Up to 20 phr, a more or less constant value is obtained but at higher loadings (30 phr and up) the property is badly affected. A similar behavior is observed for tensile strength of NR vulcanizates containing carbon black and silica. However, factors as high-surface area and/or high structure of the commercial fillers used can be associated with increased reinforcement in a rubber compound.

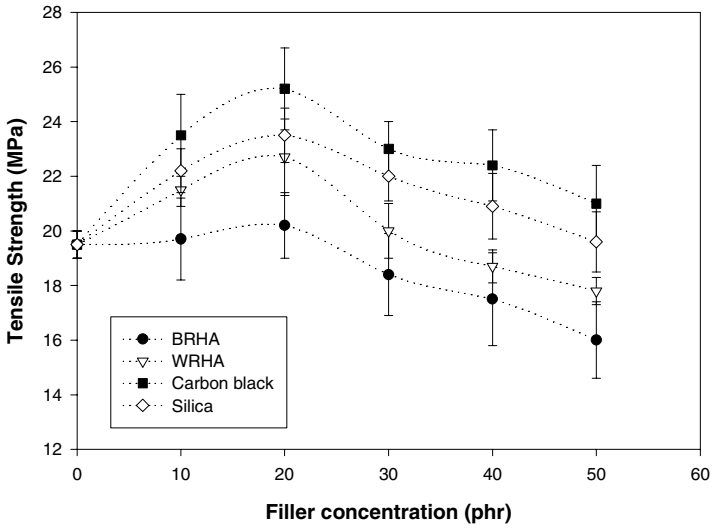

Figure 1: Tensile strength for NR compositions containing BRHA, WRHA, carbon black and silica

The factors that influence the reinforcement of elastomers by particulate fillers are: (i) the particle size or specific surface area which, together with filler loading, determine the effective contact area between filler and polymer matrix; (ii) the structure or degree of irregularity of the filler unit plays an essential role in restricting motion of elastomers chains under strain; (iii) the surface activity that is predominant factor with regard to filler-filler and filler-polymer interaction [18-20]. In our case, perhaps, the particle size of BRHA might be the main culprit for the low level of reinforcement.

According to Fetterman [19], fillers with size in the order of 50 nm, or greater, are classified as semi- or non-reinforcing. In addition, the dual nature of BRHA filler, given by the presence both silica and carbon components, with different physical and chemical properties, may also reduce the efficiency of this filler in strengthening the rubber matrix. However, the superior tensile strength of the WRHA-filled vulcanizates suggests that other factors, in addition to particle size (similar for both ashes), also influence the properties of NR vulcanizates such as surface activity and the quality of the bonding between WRHA and NR matrix.

From the SEM photomicrographs of BRHA-, WRHA, silica-, and carbon black-filled NR composites shown in Figure 2, it can be seen that the fracture surface of WRHA is more uniform compared with that of BRHA. However, the lack of intensive interactions between WRHA filler and the NR matrix is evident from these photomicrographs when they are compared with more uniform fracture surfaces of silica and carbon black vulcanizates, which are smoother because of better filler dispersion.

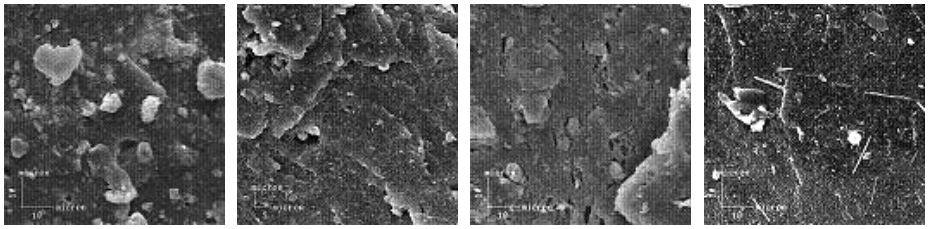

Figure 2: SEM photomicrographs of BRHA-, WRHA-, silica- and carbon black-filled NR at 20 phr filler loading after tensile fracture (x 1500)

In the Figure 3, tear strength data are presented. There is a tendency to decrease in BRHA- and WRHA-filled systems, as shown in the figure. Although, a similar behavior is observed, WRHA composites have superior values for this property, as compared with BRHA, because of their higher silica content. The formulations containing 20 phr of filler, which gave the best tensile strength results both for BRHA and WRHA, did not perform as satisfactorily as did the commercial fillers. Tear strength, like tensile strength, is affected by filler particle size and surface area. In addition, this property is controlled by the nature of the rubber and the filler, as well as by the rate and temperature of tearing [18-20]. Despite having silica content comparable to that of commercial silicas, the WRHA-filled vulcanizates are not as tear-resistant as are those containing the commercial product. Therefore, the different performances may be the result of a much more significant influence of the nature of the surface, particle size, and surface area of the filler used.

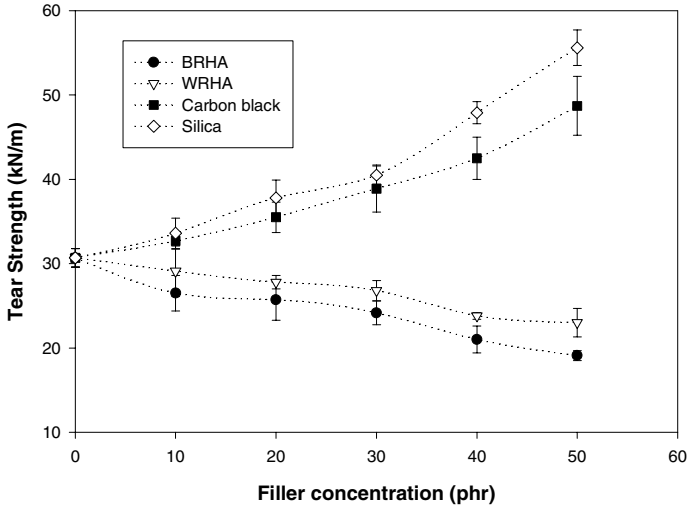

Figure 3: Tear strength for NR compositions containing BRHA, WRHA, carbon black and silica

The analysis preceding is the common form of interpretation of results described in the most of investigations about utilization of fillers in polymeric materials. The application of analysis of variance is unusual and its use can bring more information about the reinforcing effect of the fillers utilized. So, the analysis of variance was applied in the tensile strength and tear strength results of NR vulcanizates according to Tables 4 and 5 [16,17]. Tables 6 and 7 summarize the results that were found. It can be observed that in all systems of fillers, BRHA, WRHA or commercial fillers, tensile strength and tear strength are affected by filler concentration in the NR compositions since F_o values found are always greater than $f_{0.05,5,24} = 2.62$, for 95% of significance level.

Table 6: Analysis of variance for tensile strength of NR compositions containing rice husk ash and commercial fillers

Source of variation	Sum of Squares (SS)	Degrees of Freedom (DF)	Mean Square (MS)	F_o^*
BRHA	66.85	5	13.37	***11.44***
Error	28.06	24	1.17	
Total	94.91	29		
WRHA	74.70	5	14.94	***35.49***
Error	10.10	24	0.42	
Total	84.10	29		
Carbon black	89.51	5	17.90	***15.97***
Error	27.08	24	1.13	
Total	116.56	29		
Silica	65.69	5	13.14	***24.07***
Error	13.10	24	0.55	
Total	78.79	29		

$^*f_{0.05,5,24} = 2.62$, for 95% of significance level

Table 7: Analysis of variance for tear strength of NR compositions containing rice husk ash and commercial fillers

Source of variation	Sum of Squares (SS)	Degrees of Freedom (DF)	Mean Square (MS)	F_o^*
BRHA	435.01	5	87.00	***54.62***
Error	38.23	24	1.59	
Total	473.24	29		
WRHA	241.47	5	48.29	***27.60***
Error	41.99	24	1.75	
Total	283.46	29		
Carbon black	1181.71	5	236.34	***74.40***
Error	76.24	24	3.18	
Total	1257.95	29		
Silica	2155.57	5	431.12	***272.74***
Error	37.94	24	1.58	
Total	2193.51	29		

$^*f_{0.05,5,24} = 2.62$, for 95% of significance level

In the Figure 1, it was observed that BRHA is non-reinforcing filler with a little effect upon tensile strength of NR vulcanizates. It is confirmed by the analysis of variance in the Table 6 where F_o determined for BRHA-filled NR compounds is only 11.44, in other words, in the range of filler concentration of practical interest (0 up to 50 phr), BRHA imposes small modifications in the tensile strength of NR. Otherwise, carbon black that revealed reinforcing effect, as seen in Figure 1, also shows a slight influence upon tensile strength of viewpoint statistical with F_o value of 15.97. This is an indication that if reinforcement is reached at 20 phr, loadings of 30 phr and up do not more develop a positive effect. Similar observation can be done for silica-filled NR compositions, despite of F_o value. For WRHA, the analysis of variance shows an important result. As seen in the Figure 1, WRHA can be considered semi-reinforcing filler and, in the concentration range studied, F_o value found was the greater. Therefore, a variation of this filler (0 up to 50 phr) causes maximum variation upon tensile strength – an increase in the property is soon reached and, thereafter, a deleterious influence is manifested.

In the Table 7, the analysis of variance for tear strength of NR compositions containing rice husk ash and commercial fillers is summarized. From the results and according to Figure 3, at once it is observed that WRHA-filled NR compounds have the smallest F_o value and that the incorporation of WRHA in NR practically does not make difference in the tear strength. In turn, BRHA affects with more intensity this property when filler concentration changes, even if tear strength is affected of negative form. For commercial fillers, the increase observed in the Figure 3 it is justified by the analysis of F_o values. As carbon black as silica show higher values of F_o, 74.40 and 272.74, respectively. So, the incorporation and variation of concentration of these fillers not only increase tear strength but also change with rapidity the level of reinforcement.

As in all systems of fillers was observed that null hypothesis, H_o, is false, g*raphical comparison of means* and *Fisher's least significant difference* methods were used for to evaluate the differences among the treatment means.

Graphical comparison of means uses the distribution of tensile strength averages from the filler concentration experiment in relation to a normal distribution with standard deviation $\sqrt{MS_E/n}$ [16,17]. The normal distribution was sketched using a mean global of all treatments ($\overline{Y}_{..}$ in Table 4) with standard deviation represented by bars error. Since *t*-distribution looks so much like the normal, a normal curve was done with, approximately, $6\sqrt{MS_E/n}$ units wide. In the Figures 4 and 5 are shown the results for tensile strength and tear strength, respectively.

It is observed in the Figure 4 that BRHA shows little variation in the tensile strength. The mean values for each level of filler (0 up to 40 phr) are always near by mean global and/or inside of the normal curve region. Only 50 phr of BRHA could be considered filler loading really important but, as seen in Figure 1, in this level tensile strength is compromised, as discussed previously. For WRHA, NR compositions containing 10 and 20 phr of filler show a real increment in the tensile strength because of the mean values are situated outside of the normal curve and far of mean global. The other levels of filler are not important since there is not representative change in the property or the level, as 40 and 50 phr, results in lower mean tensile strength than the other treatments. Similar interpretation can be used for silica-NR filled compounds. For carbon black, it is verified that 20 phr of filler concentration

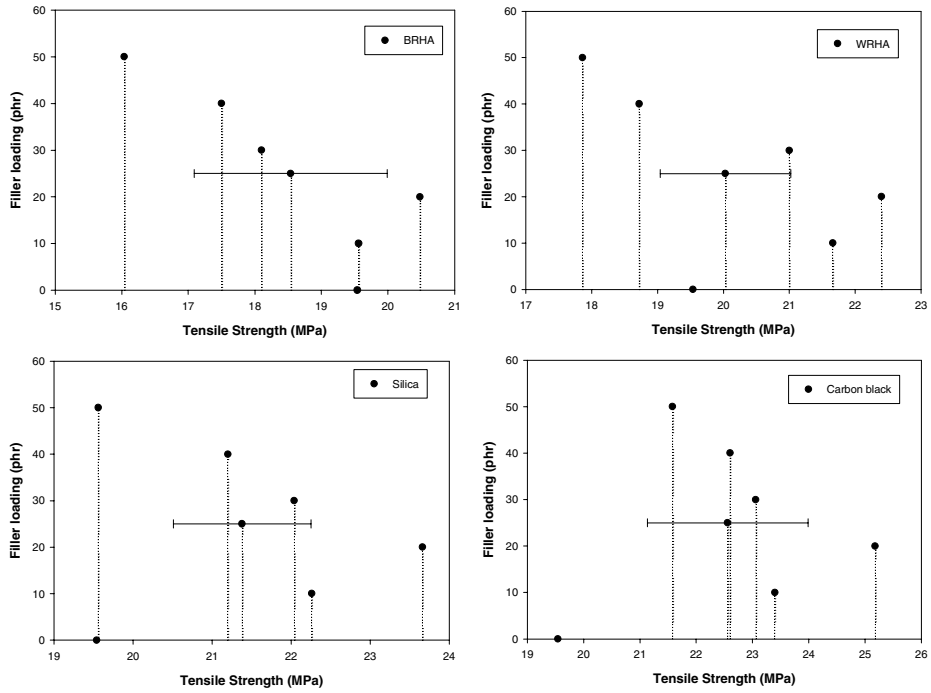

Figure 4: Tensile strength averages from the filler concentration experiment in relation to a normal distribution with standard deviation $\sqrt{MS_E/n}$

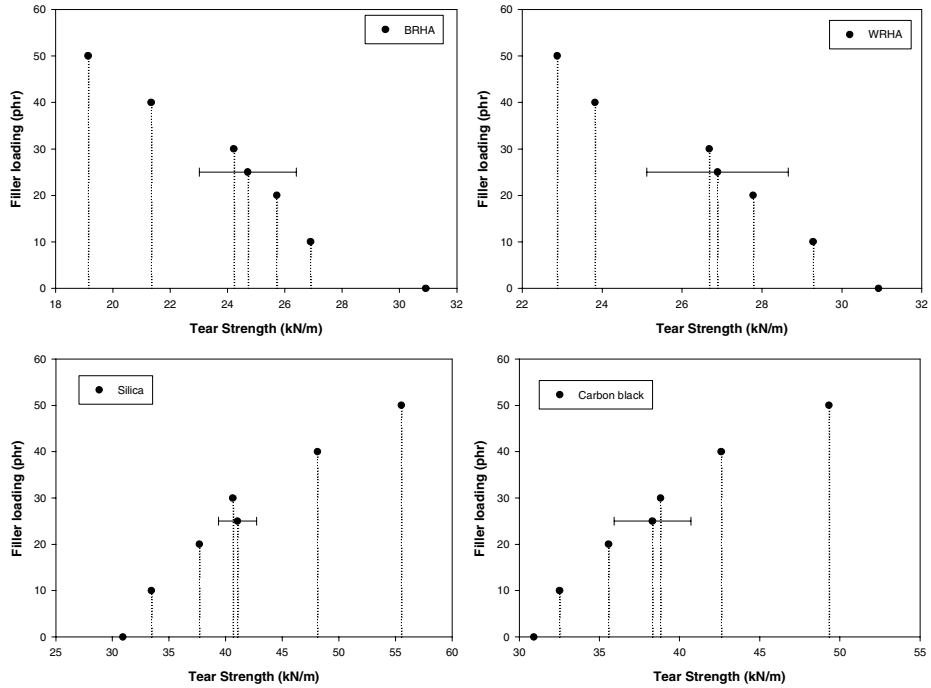

Figure 5: Tear strength averages from the filler concentration experiment in relation to a normal distribution with standard deviation $\sqrt{MS_E/n}$

represents that a maximum reinforcing effect was reached for NR compounds. Higher loadings, 30 phr and up, are not appropriate since the mean values are always around of the mean global and inside of the normal curve.

From the Figure 5, it is verified that as BRHA as WRHA show a same behavior, in other words, only NR compositions containing 40 and 50 phr exhibit mean values significant. However, in these levels, a deleterious effect is found for tear strength. So, if BRHA or WRHA is used, the incorporation can be done up to 30 phr without a compromising influence, although the mean values are small than NR pure gum. For carbon black and silica systems, it is observed that the filler concentration imposes great modifications in the tear strength, as seen in the Figure 3. As filler loading increases, there is a continuous increase in this property and the mean values move away of the mean global and normal curve.

Fisher's least significant difference compares all pairs of means with null hypothesis $H_o = \mu_i = \mu_j$ (for all $i \neq j$) using the *t*-statistic [16,17]:

$$t = \frac{\overline{y_{i.}} - \overline{y_{j.}}}{\sqrt{\frac{2 * MS_E}{n}}} \qquad \textbf{(2)}$$

Assuming a two-sided alternative hypothesis, the pair of means μ_i and μ_j would be declared significantly different if:

$$\left| \overline{y_{i.}} - \overline{y_{j.}} \right| > \text{LSD} \qquad \textbf{(3)}$$

where LSD, the least significant difference, is:

$$LSD = t_{\alpha/2,\,a(n-1)} * \sqrt{\frac{2 * MS_E}{n}}, \qquad \textbf{(4)}$$

for a = 6 treatments; n = 5 observations at each treatment; 95% of significance level; $t_{0.025,24}$ is 2.064.

In the Figures 6 and 7, the results of Fisher's LSD method for tensile strength (TS) and tear strength (TRS) are observed, respectively. The differences 1 to 5 represent the differences between 0 and 10 phr filler loading, 0 and 20 phr filler loading until 0 and 50 phr filler loading. The other differences are represented like, e.g., 35 (difference between 30 and 50 phr filler loading).

As discussed previously, BRHA does not show any reinforcing effect upon tensile strength of NR vulcanizates. In the Figure 6, it is perceptible that great differences are found for 5, 15 and 25. However, in the treatment levels 40 and 50 phr, BRHA becomes undesirable. So, once that BRHA is non-reinforcing, it can be used only up to 20 phr because of the differences 2 and 12 are below of LSD value, in other words, the mean value of tensile strength is practically the same of NR pure gum.

In the case of WRHA-filled NR vulcanizates, the differences 2, 23, 24 and 25 demonstrate that the optimum filler loading is 20 phr. For higher loadings, as tensile

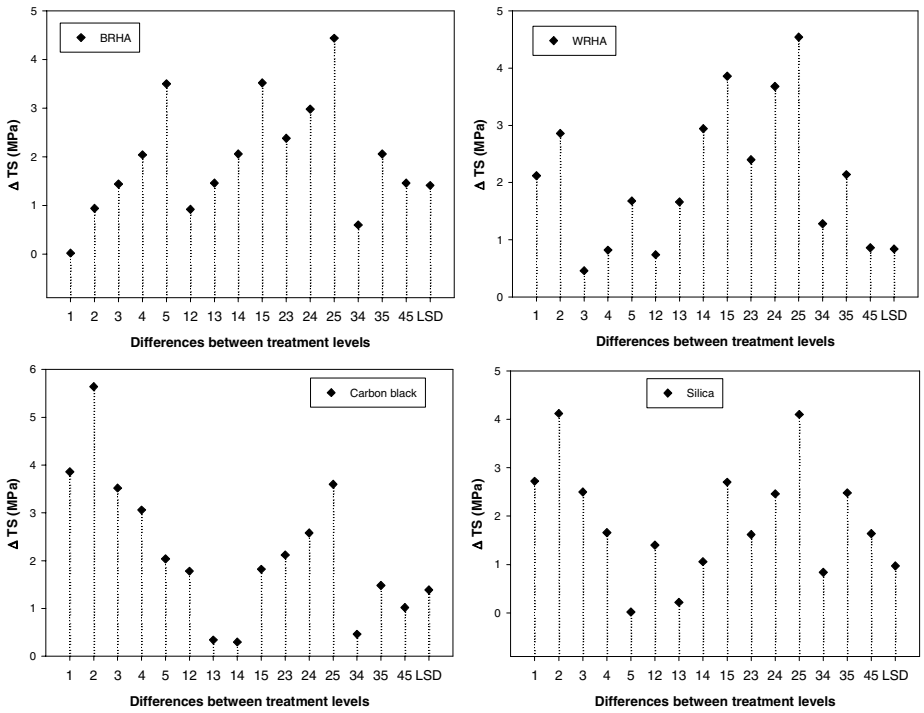

Figure 6: Results of Fisher's LSD method for tensile strength (TS)

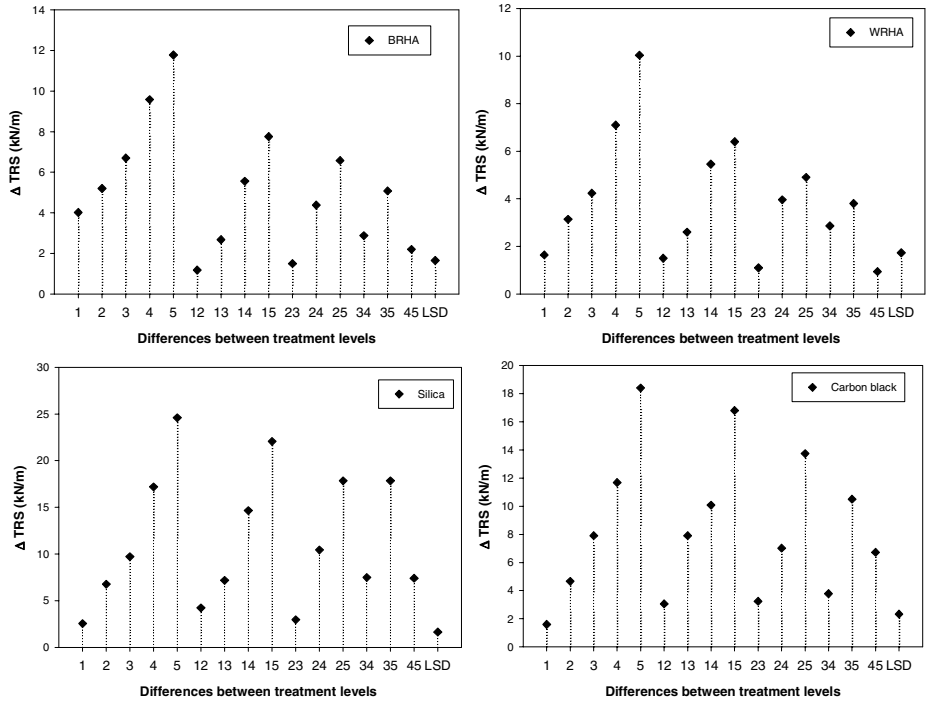

Figure 7: Results of Fisher's LSD method for tear strength (TRS)

strength is badly affected, differences like 5, 14, 15 and 35 only expose a decreasing in the property. For silica and carbon black, the observations are similar. The optimum filler loading is 20 phr, which it is confirmed by the differences 2 and 23 up to 25. Moreover, in the carbon black-filled NR compounds containing higher loadings (30 phr and up) there is small negative effects than in the mixtures containing silica in same proportion. This is confirmed by Figure 1 and by the differences 34, 35 and 45 of the Figure 6.

In the Figure 7, Fisher's LSD method is applied to tear strength. For BRHA and WRHA systems, as filler loading increases there is a progressive reduction in the tear strength, as seen in Figure 3. This is confirmed by the analysis of differences between treatment levels that are always growing and far away of LSD value, especially residues 1 to 5. For silica and carbon black systems, same behavior is also observed but the differences growing signify reinforcement upon tear strength, as seen in Figure 3.

Conclusions

Rice husk ash, BRHA and WRHA, and commercial fillers, carbon black and silica, were incorporated in the NR compositions and mechanical properties like tensile strength and tear strength were evaluated. Concerning the mechanical properties, the results show that the tear strengths of BRHA-, WRHA-, carbon black-, and silica-filled NR compounds are very similar for low filler loadings; regarding tensile strength, BRHA is not as efficient as the commonly used fillers carbon black and

silica. As for WRHA, in spite of parameters such as surface area and particle size, the vulcanizate with 20 phr of this filler, which gave the best result, showed tensile strength not much inferior to commercial carbon black- or silica-filled vulcanizates. For tear strength, as for BRHA and WRHA, they not show reinforcement in comparison with the effect of commercial fillers.

The analysis of variance was also applied for evaluation of the effect of rice husk ash (BRHA and WRHA) and commercial fillers (silica and carbon black) in the NR compositions. The analysis showed importance since not only the observations about the mechanical properties were confirmed but also new informations were obtained.

The analysis reveals that BRHA shows little variation in the mechanical properties of NR compounds, in other words, it is non-reinforcing filler and their use must be restricted to 20 phr, approximately. For WRHA, NR compositions containing 10 and 20 phr of filler show a real increment in the tensile strength and the variation of this filler (0 up to 50 phr) causes maximum variation upon tensile strength, according to F_o value. Carbon black and silica develop reinforcing effect upon the mechanical properties but, of the viewpoint statistical, in the tensile strength, this reinforcement is only reached in 20 phr. High loading, 30 phr and up, does not any difference.

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