



MECHANICAL EVALUATION OF A HYBRID NITRILE RUBBER COMPOSITE MADE WITH COARSE PARTICLES OF PUMPKINS SEED HUSK, SILICA AND SILANE COUPLING AGENT

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ABSTRACT

Acrylonitrile-butadiene rubber (NBR) composites were developed with hybrid filler from silica and coarse particles of pumpkins seed husk (PSH). Bis (triethoxy-silylpropyl) tetrasulfide (TESPT) was used as coupling agent. Other ingredients used: polar plasticizer, antioxidant, aid process and sulfur curing system. PSH was mercerized with dilute NaOH solution. The compounding was carried out in a laboratory size two-roll miller; the TESPT was added directly in the mixing stage. The rubber composites were vulcanized using compression molding in a laboratory press. Four NBR vulcanizates were made to evaluate the effect of mercerized PSH and silane on the mechanical properties. It was found that the incorporation of PSH affected the curing characteristics, hardness, tensile strength, elongation at break and abrasion resistance in hybrid composites. The presence of TESPT in the hybrid compound improved the tensile and elongation properties. However, the presence of large PSH particles probably limited silane's performance on other properties. PSH is a waste of seeds husk from pumpkin fruits (genus *Curcubita*). Fine PSH particles can be an alternative to elaborate hybrid rubber compounds since it allows achieving a good balance between mechanical properties and friendly environmental production.

Keywords: composites, pumpkins seeds, mercerization, nitrile rubber, silica, silane, TESPT.

INTRODUCTION

Natural fibers and wood sawdust, named vegetable fillers (VF) have emerged as fillers in widely polymeric composites to manufacture parts in automotive, construction, furniture, home and others industries. The features of VF such as lightweight (specific gravity: 0.8-1.6) [1, 2], superior mechanical properties, less cost of production and sustainable source makes them attractive for partial replacement of polymers and mineral fillers [2, 3]. VFs improve stiffness, hardness, modulus and strength to rubber composites [4].

The main disadvantages of VF in polymeric composites are poor dimensional stability and high hydrophilic nature, which generates incompatibility with polymeric matrix, mostly hydrophobic nature [5]. The interfacial bonding between the fiber and matrix affects the mechanical performance of composites [6].

To improve the fiber-polymer interfacial adhesion there are several strategies, from surface chemical treatments of fibers to use of compatibilizer agents. The mercerization of the natural fibers [7] is considered an important initial treatment but not sufficient, this modification removes hemicellulose, wax layers generate surface roughness, improve thermal properties [8] and exposes the -OH groups, so that these sites can react later with chemical agents, such as silane coupling agent (SCA) [7, 9], anhydride maleic [10], acrylics [7], maleated polyolefins [11-14], maleated and epoxidized natural rubber [15-17] to create covalent bonds in particle-polymeric matrix.

Rubber reinforcement improves mechanical properties such as modulus, tension, tear, abrasion resistance, compression, stiffness, hardness and dynamic properties [18, 19]. Carbon black [20] and silica are the two main reinforcing fillers. Silica outperforms carbon black in reducing the rolling resistance of tire tread and saving energy [21].

The combination of VFs with reinforcing agents to form hybrid fillers has become important because it allows balancing mechanical, physical, thermal, water absorption, acoustic, dynamic, among others properties, could reduce overall cost, and manufacture environmentally friendly polymer composites [8, 22, 23]. The VFs-silica hybrid filler causes issues in compounding process due to the difficult dispersion in rubber matrix.

Synthetic silicas have siloxane and silanol groups acids [18, 24], which form agglomerates that are difficult to break, do not allow a real interaction of the particles with the non-polar rubbers, the silanol groups interact with the basic accelerators, causing long cure times and slow cure rates [24]. In order to develop interfacial bonding of VFs and silica with rubber matrix, therefore leading to an increase the crosslink density thermal stability and mechanical properties of rubber composites, SCA are used [18, 25]. Chemical bonds are formed between hydroxyl and silanol group of the fillers and alkoxy groups of SCA. Consequently, rubber chemisorption on the surface of filler increases and rubber exhibits increased hardness and mechanical strength [26].

Silicas and natural fibers are dipped in hydrolyzed silane alcohol solution followed by washing



and drying. Surface treatment on silica reduces decrease of the hydroxy groups through siloxane or hydrogen bonding at the interfaces between silicas and silane coupling agents [18, 24]. In silanized natural fibers, the $-OH$ groups have been modified by $-Si-O-Si-$ bonds, increasing the hydrophobicity of the particle [9]. Cao *et al.*, [27] carried out surface treatment of silica with hydrolyzed TESPT and graphene oxide con with (3-aminopropyl) triethoxysilane (APTES), forming a hybrid with latex, once dry, it was added in to the natural rubber matrix to develop the tire-tread of superior properties. Park and Cho [18] tested the surface treatment of silica with different hydrolyzed SCAs: γ -aminopropyl triethoxysilane, γ -chloropropyl trimethoxysilane and γ -methacryloxypropyltrimethoxysilane, the rubber composites SBR/(40phr silanized silicas) showed an increase of crosslink density, thermal stability and mechanical properties. Masłowski [28] developed a functional hybrid filler from flour straw silanized and silica, the presence of the lignocellulosic material (into flour straw) improved the thermal stability, barrier properties and flammability of the natural rubber (NR) vulcanizates. In another investigation [29] bagasse fiber ash and silica were treated with SCA to improve the reinforcement of NR compounds. In the rubber industry process, SCA is added directly to rubber/silica mix [30–32], this way is an alternative method for the coupling of rubbers with VF [33].

NBR is a polar rubber, it is used to produce technical devices due to its high resistance against oil, fuel, chemicals and low permeability for non-polar gases [19, 34, 35]. The similar polarity of NBR and natural fibers is key to design compounding strategies. Hariwongsanupab *et al.*, [36] developed a method to disperse short pineapple leaf fiber in NBR, this blend in a next step was mixed with NR, despite the fact that the two rubbers are immiscible, it was found that significant improvement of the stress transfer in the low strain region can be obtained. Chukwujike *et al.*, [37] reported an increase of mechanical properties by partially replaced NR by NBR in carbonized corn hub powder composites.

In this study, composites of NBR with hybrid filler: (silica+seed husks pumpkin) were prepared, TESPT was used to improve coupling of the dispersed phase with the rubber matrix. The effect of natural fiber and silane were analyzed by measuring the cure and mechanical properties of compounds. The seeds are obtained from the waste of *Cucurbitasp* fruits, pumpkins are an important global food source [38].

EXPERIMENTAL

Materials

Pumpkins seeds were collected from local farms (Colombia). NBR (39% acrylonitrile), Perbunan[®] N3945 made by Arlanxco[®] (Brazil). Synthetic silica, Rubbersil[®] RS200 with BET of 185 m²/g from Glassven[®] (China). Plasticizer butyl benzyl phthalate (BBP), Unimoll BB[®] manufactured by Arlanxco[®] (Brazil). Coupling agent TESPT Si-69[®] was supplied by Evonik[®] (Colombia). Process aid, Struktol WB16[®], from Struktol[®] (USA). Non-staining antioxidant, Vulkanox SP[®] from Lanxess[®] (Brazil). Zinc oxide (gold seal) was supplied by Metalox[®] S.A. (Colombia). Micronized sulfur mesh 325, from Asuagro[®] S.A.S. (Colombia). Accelerators: Perkacit[®]-TMTD, Perkacit[®]-MBTS, Perkacit[®]-MBT, manufactured by Flexsys Chemicals[®] (Brazil). Reagents for mercerization: NaOH, acetic acid and deionized water were purchased from the local chemical supplier.

CHS Treatments

First, pumpkins seeds were cut into 5-10 mm pieces to remove the cotyledon, then the husk was ground in a blade mill, the particles was sieved on a mesh between 0.8-2.2 mm diameter.

The mercerization was carried out by immersing the PSH in NaOH solution (4% w/w) for three hours at 40 °C (Figure-1-a), then PSH was washed with acetic acid solution (1% w/w) and deionized water to neutral pH. PSH was dried in laboratory oven at 100 °C for 24 hours (Figure-1-b).



Figure-1. a) PSH, mercerization; b) PHS, drying; c) Compounding of NBR/silica/PSH composites.

NBR Composites: Compounding

Four compounds were made (Table-1). All blends were formulated with 20 parts per hundred rubber (phr) of plasticizer, 50 phr of silica and same quantities of curatives. PSH and TESP were varied. The acronyms to

name the compounds were: rubber+silica (NBR/silica); rubber + silica + silane (NBR/silica-_{TESPT}); rubber+silica + PSH (NBR/Hyb) and rubber+silica+PSH+silane (NBR/Hyb-_{TESPT}), where the Hyb denotes the hybrid filler. The rubber blends were made in a laboratory size two roll-



mill with a friction ratio of 1.42; diameter and length of cylinders: 14 cm and 32 cm respectively, nip: 2-3 mm.

Table-1. Formulations of NBR composites.

Ingredients	NBR/silica	NBR/silica _{.TESPT}	NBR/Hyb	NBR/Hyb _{.TESPT}
NBR	100	100	100	100
Silica	50	50	50	50
PSH mercerized			25	25
Plasticizer	20	20	20	20
TESPT		2.0		2.0
Antioxidant	1.0	1.0	1.0	1.0
ZnO	5.0	5.0	5.0	5.0
Process aid	1.2	1.2	1.2	1.2
MBTS	1.2	1.2	1.2	1.2
MBT	1.2	1.2	1.2	1.2
TMTD	0.2	0.2	0.2	0.2
Sulfur	2.0	2.0	2.0	2.0

The mixing was carried out in three steps: First, NBR was milling 1/3 part of the silica was added then the silane was placed into blend, later the 2/3 parts of silica and PSH were incorporated. Second stage: the rollers were heated up to 110 °C, then the mixtures were homogenized for 10 minutes to ensure silanization, the blends remained at rest 24 hours. Third step: the incorporation of additives and curatives was carried out in the mill at 65 °C, then composites were homogenized and laminated. All composites were made following the same procedure to ensure uniformity.

All specimens were obtained by compression molding, a laboratory electric heating press was used, the rubber composites were at 160±1 °C. The tensile and tear specimens came from vulcanized sheets in a mold with an area 16×16 cm², thickness 3.45 mm and cure time 5 minutes. Sheets for hardness and abrasion resistance were vulcanized inside a mold with area 8×8 cm², thickness of 6.2 mm and cure time 10 minutes. The specimens for compression set were obtained from vulcanized cylinders, the mold dimensions were: diameter 28 mm and height: 14.2 mm, the vulcanizing time was 16 minutes.

Cure properties of rubber blends were determined according to ASTM D2084-17 using an oscillating disk rheometer Monsanto[®] MDR 2000TM (USA). Rheometric curves were run at 160 °C and 5 minutes.

NBR Composites: Determination of Mechanical Properties

Tensile strength and elongation at break were carried out according to the standard ASTM D412-06A [39], specimen with C geometry was used. Tear strength was made by applying the standard ASTM D624-00 [40], specimen type B was used. Tensile and tear specimens were cut from vulcanized sheets; the tests were carried out

in Shimadzu[®] AGS-X (USA) universal testing machine. Testing parameters cross heat displacement speed: 100 mm/minute; temperature: 23 °C, relative humidity: 50±1%. Four specimens of each composite were tested. Morphology of fractured surface (specimens from tensile test) was observed by scanning electron microscopy (SEM) in JEOL200[®] (USA). Surface metallization of samples was carried out on the Balzers[®] SDC 050 (USA) with a gold-palladium film of ± 5nm of thickness.

Abrasion resistance was measured according to ASTM D5963-04[41], B-method (rotating test piece). An abrasimeter Kejian3025[®] (China) was used, four specimens of each composite were tested. Compression set under constant deflection was measured according to ASTM D395 [42], B-Method, four specimens/composite were tested. Hardness was carried out following to ASTM D2240-15, the durometer Shore A-Insizer[®] was used, four measurements/composite were made. Specific gravity were performed according to ASTM D792-13[43] Method A.

EXPERIMENTAL DESIGN

To determine the influence of PSH and TESPT on the mechanical properties, 1×4 experimental design was carried out, means were compared using one-way ANOVA. Where: the factor was the formulation, the levels (four composites), output variables (six mechanical properties). The hypotheses proposed were: H₀: The means of levels are equal; H₁: At least one of the level means is different.

The statistical model was validated by the application of the Shapiro-Will test for the 24 observations sets (6 output variables × 4 levels). The null and alternative hypotheses were defined: H₀: The observations correspond to a normal distribution; H₁: The observations



do not correspond to a normal distribution. Levene's test was performed to contrast the homogeneity of variances to validate the ANOVA model. The null and alternative hypotheses were defined: H_0 : The variances are equal; H_1 : At least one of the variances is different. One-way ANOVA was used to compare the means of rubber composites determine if there were significant differences between them. Two hypotheses were raised: the null hypothesis (H_0): There is no difference among group means; the alternate hypothesis (H_1): At least one mean differs significantly from the overall mean of the dependent variable.

HSD was applied for the multiple contrast of means. The Tamhane test was applied in cases where the ANOVA was not valid. Statistical analyzes were carried out with a statistical confidence level of 95%, the SSPS[®] software was used.

RESULTS AND DISCUSSIONS

Morphology of Fillers

The Figure-2 shows the morphology of silica and PSH, with obvious differences in size, morphology and

geometry between them. The silica-RS200[®] particles have an average diameter of 5 μm according to technical sheet, its small particle size is key to reinforcement. The silica particles (Figure-2-a) are spherical with small agglomerations, which are formed by the presence of high silanol groups on its surface, these polar groups promote strong filler-filler interactions leading to high degree of aggregation and agglomeration of silica particles [44], the aggregated particles can break by shear action of mixing. PSH mercerized particles are 300-500 times larger than silica, with average diameters between 1500-2000 microns, therefore PSH is not flour, it is considered a coarse particle filler. PSH particles had irregular size and geometry similar to sheets, cubes or prisms (Figure-2-b), showed surface roughness due to mercerization. The presence of coarse particles into polymeric matrix does not allow homogeneity of the blends, around them the stresses are concentrated producing failures, leading to a weakening of the mechanical performance of the rubber composites. The size of particle can influence mechanical properties of polymeric composites [45].

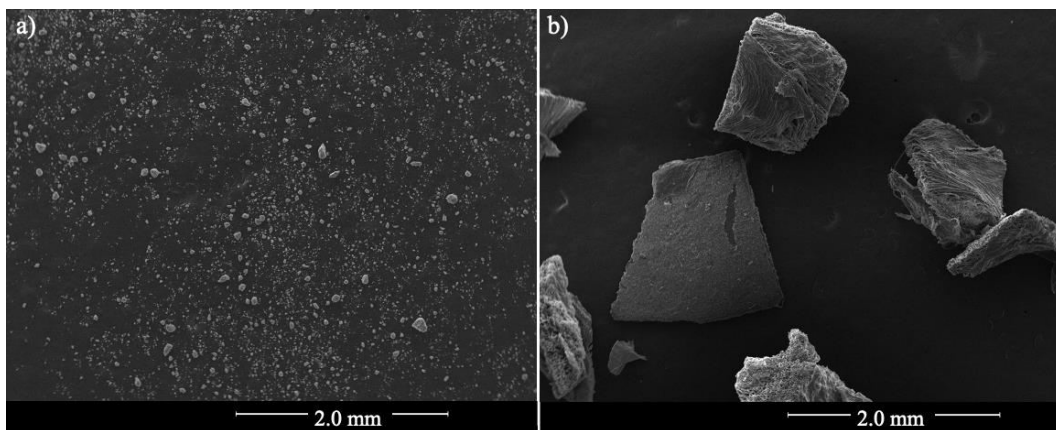


Figure-2. SEM 50x of particles: a) Silica; b) PSH mercerized.

Curing Behavior

The presence of silane and fiber affected the curing characteristics of the mixtures (Figure-3). Minimum torque (M_L) is related to viscosity of the SBR blends before vulcanization, if the viscosity increases significantly the process of mixing and cure becomes more difficult [24, 46].

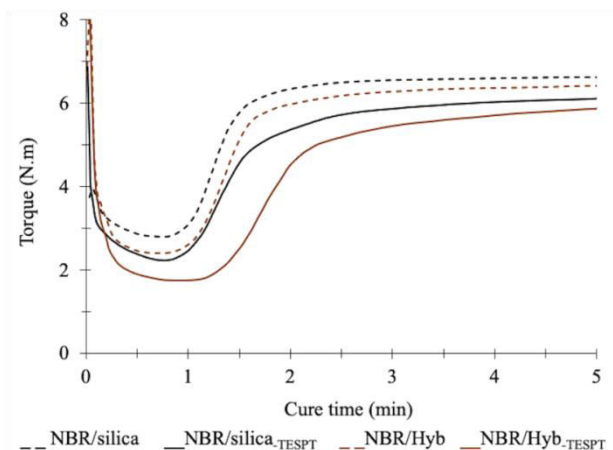


Figure-3. Rheometric curves of NBR blends.



The addition of 25 phr of PSH and 2 parts of TESPT decreased the M_L (Table-2). In fact, the M_L of the NBR/Hyb compound was 20.0% lower than that of NBR/silica; NBR/silica- $_{TESPT}$ was 20.4% lower than NBR/silica, while the lowest value was for NBR/Hyb- $_{TESPT}$, which was 22.3% lower than NBR/Hyb. PSH caused a decrease in the M_L , the coarse particles likely separated the polymer chains due to the low interfacial adhesion and in this way facilitated an easier movement of them. The addition of silane decreased the M_L , probably the silane had a behavior slightly like a “plasticizer” because TESPT is a liquid.

Maximum torque (M_H) is related to stiffness, crosslinking density of the rubber vulcanizates [46]. A direct relationship of M_H with M_L was observed in NBR blends, $>M_H: >M_L$ (Figure-3). The highest value was obtained for NBR/silica, the addition of PSH slightly decreased the M_H by 3.2%. The composites with silane have lower M_H values. NBR/silica- $_{TESPT}$ and NBR/Hyb- $_{TESPT}$ decreased M_H by 7.8% and 8.4% compared to NBR/silica and NBR/Hyb respectively. Hybrid compounds were expected to have the highest M_H values, since the natural fibers impart stiffness, probably the presence of coarse particles did not restrict molecular movement. The more inclusion of filler leads to limited molecular motion resulting in harder and more rigid compounds [33].

Table-2. Cure characteristics of NBR composites.

Composite	M_L (Nm)	M_H (Nm)	t_{S2} (min)	t_{90} (min)
NBR/silica	2.80	6.63	0.97	4.97
NBR/silica- $_{TESPT}$	2.23	6.11	1.00	2.55
NBR/Hyb	2.24	6.42	1.00	2.09
NBR/Hyb- $_{TESPT}$	1.74	5.88	1.28	3.68

Scorch time (t_{S2}) indicates when the rubber begins to cure. No significant differences were observed for t_{S2} of NBR/composites except for NBR/Hyb- $_{TESPT}$ where, the addition of PSH and TESPT produced a t_{S2} by 28%. Regarding TESPT, this result was not expected, since silanes reduce t_{S2} in NR composites [26,44].

The t_{90} is the time for completion of cure a 90% at certain temperature, the 10% of curing is completed with the remaining heat of the piece removed from the mold [46]. The presence of the silane in NBR/silica- $_{TESPT}$ shortened the t_{90} by 48.7% with respect to NBR/silica, this result agrees with those published by other researchers [26, 44]. However, the opposite effect was obtained in the hybrid (Table-2), t_{90} of NBR/Hyb- $_{TESPT}$ was 20% delayed to NBR/Hyb.

Statistical Model Validation

The results of the Shapiro-Wilk test are shown in Table-3, as the p-value is greater than 0.05, then the null hypothesis is not rejected. The data are normally distributed.

Table-3. Shapiro-Wilk test, df: 4.

Composite	Tensile strength	Elongation	Tear strength	Abrasion resistance	Compression set	Hardness
NBR/silica	0.797	0.293	0.468	0.735	0.463	0.067
NBR/silica- $_{TESPT}$	0.953	0.454	0.134	0.976	0.505	0.114
NBR/Hyb	0.623	0.295	0.967	0.976	0.279	0.408
NBR/Hyb- $_{TESPT}$	0.309	0.784	0.463	0.955	0.577	0.178

Table-4 shows the results of the test of homogeneity of variances. As the p-value for Levene's test was more than 0.05 the H_0 was accepted (all variances are equal) except for output variable Tensile strength (valor-

$p < 0.05$), therefore for this last variable one-way ANOVA was not valid. The results of the one-way ANOVA test are shown in Table-5. In all the output variables p-value was less than 0.5, therefore the H_0 was rejected.

Table-4. Levene's test based on mean, df_1 : 3; df_2 : 12.

	Tensile strength	Elongation	Young's Modulus	Tear strength	Abrasion resistance	Compression set	Hardness
Levene Statistic	8.101	1.757	0.272	0.133	1.099	0.003	1.103
p-value	0.003*	0.209	0.364	0.939	0.387	1.000	0.114

**Table-5.** One-way ANOVA.

Output variable	Source of variance	SS	df	MS	F	p-value
Elongation	Between groups	227328.005	3	75776.002	66.231	0.000
	Within group	13729.335	12	1144.111		
	Total	241057.340	15			
Young's Modulus	Between groups	0.276	3	0.092	426.473	0.000
	Within group	0.003	12	0.000		
	Total	0.279	15			
Tear strength	Between groups	1195.145	3	398.302	81.636	0.000
	Within group	58.560	12	4.880		
	Total	1253.705	15			
Abrasion resistance	Between groups	35580.922	3	11860.30734	343.071	0.000
	Within group	414.852	12	34.571		
	Total	35995.774	15			
Compression set	Between groups	158.604	3	52.868	9.754	0.002
	Within group	65.040	12	5.420		
	Total	223.643	15			
Hardness	Between groups	1066.278	3	355.426	251.329	0.000
	Within group	39.597	12	1.414		
	Total	1105.875	15			

Table-6 shows the Tukey's multiple comparison test, except for the tensile strength (valor- $p < 0.05$, Levene' test) where the Tamhane test was used.

Tensile Properties

Tensile strength

The stress-strain curve (Figure-4-a) shows that at low strain (0-50%) the composite behavior was determined by the PSH and at the high elongation by silica, this performance is characteristic in vulcanized

rubber formulated with reinforcing filler and natural fibers [47].

The incorporation of 25 phr of mercerized PSH significantly decreased the tensile strength value (NBR/Hyb, 8.95 MPa), equivalent to a 13.8% drop respect to NBR/silica (Figure-3-b). The PSH coarse granules (Figure-2-b) behaved as agglomerations within the rubber matrix, therefore a homogeneous dispersion of particles was not achieved, this led to a concentration of stress resulting in an early failure of the composite exposed to tensile test.

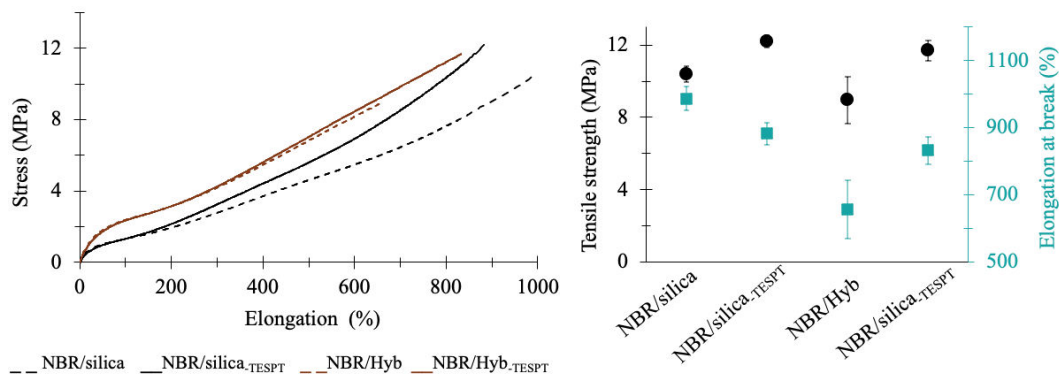
**Table-6.** Tukey's multiple comparison test.* Significant differences.

I	J	Tensile strength ^T		Elongation		Tear strength		Abrasion resistance		Compression set		Hardness	
1	2	0.001	*	0.004	*	0.000	*	0.000	*	0.087		0.098	
	3	0.188		0.000	*	0.973		0.018	*	0.177		0.000	*
	4	0.008	*	0.000	*	0.318		0.872		0.316		0.000	*
2	1	0.001	*	0.004	*	0.0000	*	0.000	*	0.087		0.098	
	3	0.018	*	0.000	*	0.000	*	0.000	*	0.002	*	0.000	*
	4	0.307		0.219		0.000	*	0.000	*	0.004	*	0.000	*
3	1	0.188		0.000	*	0.973		0.018	*	0.177		0.000	*
	2	0.018	*	0.000	*	0.000	*	0.000	*	0.002	*	0.000	*
	4	0.021	*	0.000	*	0.536		0.067		0.978		0.997	
4	1	0.008	*	0.000	*	0.318		0.872		0.316		0.000	*
	2	0.307		0.219		0.000	*	0.000	*	0.004	*	0.000	*
	3	0.021	*	0.000	*	0.536		0.067		0.978		0.997	

^TTamhane's test. 1(NBR/silica); 2(NBR/silica-_{TESPT}); 3(NBR/Hyb); 4(NBR/Hyb-_{TESPT})

The strength of the composites decreases due to the presence of large and irregular particles, which are unable to resist stresses transferred from the polymer matrix [26]. Li reported that tensile strength decreased as particle size

increased, the tensile strength was 6.13 MPa (ϕ particle, 3.4 μ m) and 3.98 MPa (ϕ particle, 57 μ m), smaller particle size offers better dispersion [45].

**Figure-4.** a) Stress-elongation curves. b) Tensile strength and elongation at break.

The presence of TESPT improved the tensile strength of the compounds formulated with silica and natural fiber. The tensile strength of NBR/silica-_{TESPT} (12.2 MPa) was 17.4% higher than NBR/silica, this result was expected, since silanes is designed to improve filler/polymer interfacial bond, achieving an increase of tensile strength. Chandra *et al.* [30], reported that addition of 2 phr of TESPT increase of tensile strength from 23.97 MPa to 31.1 MPa in NR/(20 phr silica) composites. Katueangngan *et al.* [44], concluded that tensile strength was greater in NR/silica composites treated with TESPT than non-silane treated samples, because coupling agent promoted higher crosslink density and rubber-filler interaction. In silica-silane system, the TESPT can form covalent bonds with the silica surface via the silanization

reaction between the ethoxy group of TESPT and Si-OH groups of silica and create crosslinks with the rubber phase, this is the basis for the overall performance of mechanical properties in silica-silane systems [30].

The presence of the TESPT in the hybrid composite increased the tensile up to 11.7 MPa, being 30.7% higher than NBR/hyb. The silane probably improved the interaction of silica and PSH with the NBR matrix. The TESPT is believed to improve the surface functionality of the natural fibers and subsequently enabled them to bond chemically to the rubber matrix [26]. Several studies demonstrated the positive action of silane to improve the mechanical performance of rubbers filled with natural fibers [33]. Daud *et al.* [33], observed an increase in tensile strength up to 59.3% when adding



1phr of APTMS silane to NR/(20 phr of palm kernel powder) composites, without APTES tensile strength was 11.74 MPa. They mention that in tensile test, molecular chain break and stress is transferred to adjacent number of other chains via filler particles, as a result, the composites resist detachment as the filler attached strongly to rubber matrix by the presence of silane. No significant differences in tensile strength were found NBR/Hyb_{TESPT} and NBR/silica_{TESPT} (Table-6).

Elongation at break

The PSH and TESPT caused significant differences in the elongation at break means (p-value 0,000 Table-5). Elongation at break decreased due to the presence of fiber (Figure-3-b), a value of 657.3% was reported for NBR/Hyb (Figure-4-b), equivalent to a significant decrease (Table-6) of 30% respect to NBR/silica. The decrease in elongation is related to the tensile analysis: large PSH particle size and poor interfacial adhesion, however the elongation at break values above 600% are very good for most applications.

The presence of TESP in NBR/silica_{TESPT} and NBR/Hyb_{TESPT} had the opposite effect. The elongation at break value reported for NBR/silica_{TESPT} was 882% being 10.6% lower than NBR/silica. The silica-TESPT-rubber interaction induces a restriction in the mobility of the chains (stiffening) leading to a decrease in elongation at break [30, 33].

In contrast, the NBR/Hyb_{TESPT} had an increase in elongation at break up to 832.6% being 26.7% higher than NBR/Hyb, the TESPT promotes better dispersion of the PSH and interfacial adhesion between particle and rubber, in this way, the transfer of stress was improved from rubber to particle. A similar result was reported by Daud *et al.* [33], the NR/(20 phr of palm kernel powder) with 1 phr of TESPT had 847.8% of elongation at break against 747.2% (without silane).

Tensile Test, Surface Fractured Morphology of NBR Composites-Morphological Analysis

The Figures 5-6 show SEM images the fractured surfaces of the NBR composites after tensile test.

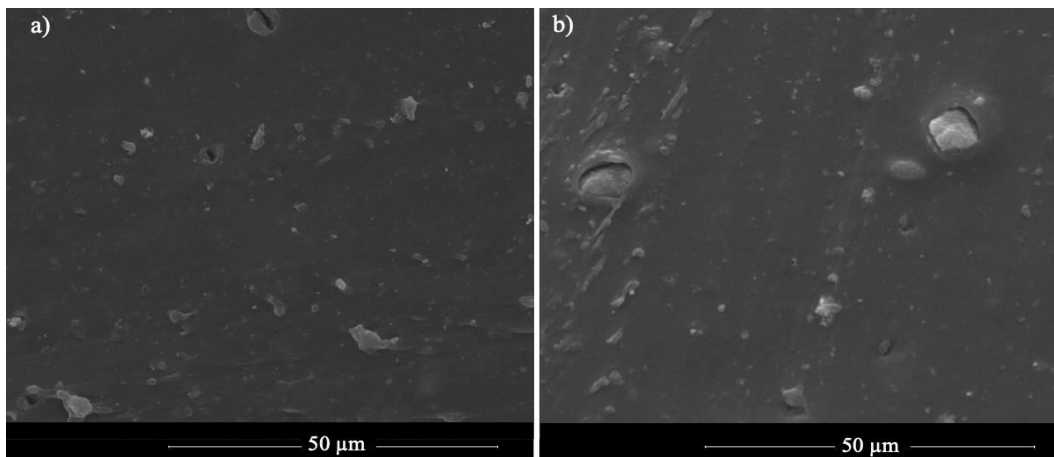


Figure-5. SEM 50X. Fractured surfaces: a) NBR/silica; b) NBR/silica_{TESPT}.

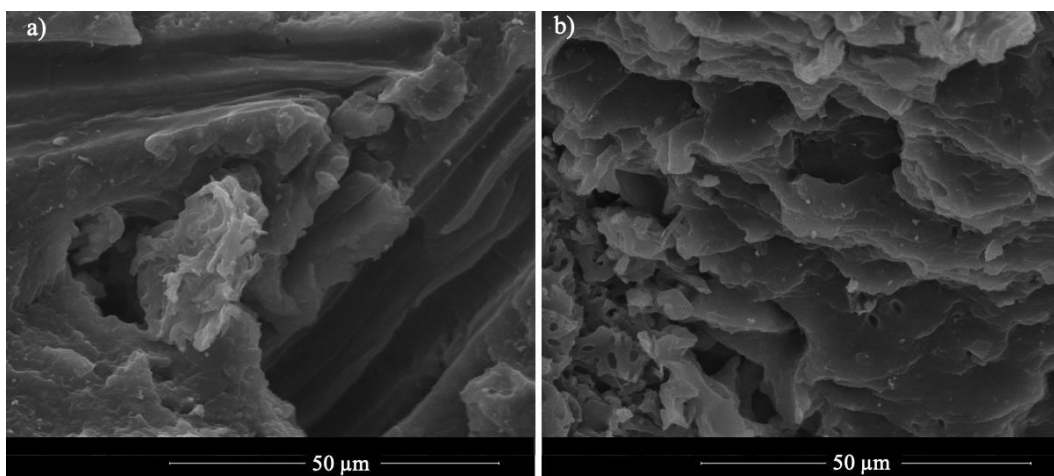


Figure-6. SEM 3000X. Fractured surfaces: a) NBR/Hyb; b) NBR/Hyb_{TESPT}.



The fractured surfaces of the NBR/silica and NBR/silica_{-TESPT} composites (Figures 5-a-b) were homogeneous, smooth, with the presence of some small silica agglomerations. Therefore, there is evidence of a strong interaction silica-NBR. The silica agglomerates remain attached to rubber matrix (Figure-5-b).

The surfaces of the hybrid compounds show a completely irregular morphology; large voids are observed as a result of the pull out of PSH particles. The holes are the places where the composites failed, they also show the loss of stress transfer and low interfacial adhesion PSH-rubber, leading to a decrease in tensile properties. The

Figure-6-a shows particle that were not wetted by the rubber, since it is a coarse particle. The white points (Figure-6-b) correspond to silica particles, comparatively the enormous difference in size between both charges is observed.

Tear strength

Tear strength measures the ability of rubber to resist an incision (stress concentration). The addition of PSH did not affect the tear strength; 58.1kN/m was reported for NBR/Hyb (Figure-7), which did not present significant difference with respect to NBR/silica.

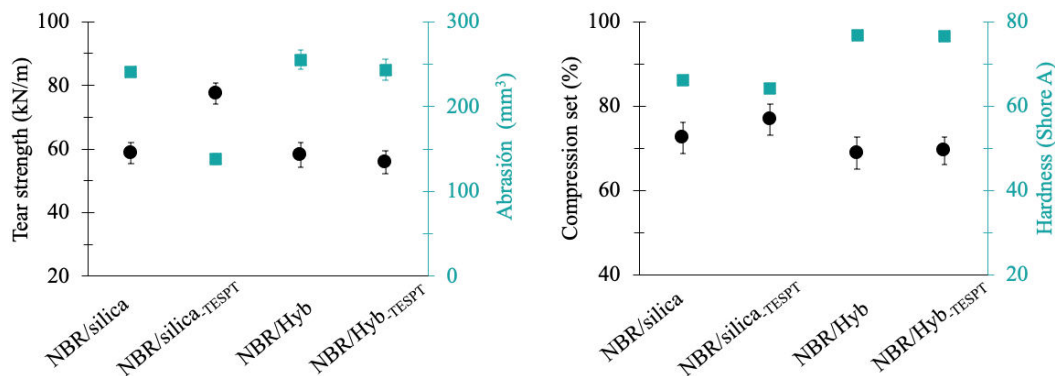


Figure-7. Tear strength, abrasion resistance, compression set and Hardness of NBR vulcanizates.

The presence of TESPT had a positive effect on the rubber composite formulated with silica. In fact, the highest tear strength was for NBR/silica_{-TESPT} (77.4kN/m), being 31.7% higher than NBR/silica. TESPT increased tear strength because it contributes to improve the dispersion and rubber-silica interaction [24][30]. TESPT had no significant effect on the hybrid composite (Table 6), tear strength was 55.9kN/m for NBR/Hyb_{-TESPT}; the coarse particles of PSH likely limited the performance of the silane. Opposite result was reported by Ismail *et al.* [26], the tear strength was 27 kN/m in NR/(30 phr bamboo fibre) with TESPT, which was 50% higher than NR composite without silane.

Abrasion resistance

Less volume loss in the test means greater resistance to wear. The presence of PSH and TESPT significantly affected abrasion resistance (p-value 0.000, Table-5). The value of NBR/Hyb was 255.2 mm³ (Figure-7), being slightly lower by 6.2% in abrasion resistance compared to NBR/silica.

TESPT improved the abrasion resistance of the compound formulated with silica. Indeed, the value of NBR/silica_{-TESPT} was 138.3 mm³; this composite presented the highest resistance, which is 42.5% better than NBR/silica. This result was expected, since silane is used in the rubber industry to improve properties such as resistance to abrasion.

The addition of the silane to the hybrid compound had no effect on abrasion resistance. There were no differences in the means of El NBR/Hyb and El

NBR/Hyb_{-TESPT} (Table-6). Better silane behavior was expected in the hybrid compound, likely the wear produced a detachment of the coarse particles together with the polymer around them, limited silane performance.

Compression set

All NBR composites had poor compression set performance; the values were in the range of 70-77% (Figure-7). The design of the formulations (Table-1) is directly related to the results, the presence of 20 phr the plasticizer and the use of a conventional vulcanization system had a negative influence. Efficient vulcanization (EV) curing systems are recommended for optimal results of compression set.

However, it was observed that the incorporation of PSH had no effect on property (Figure-5-b and Table-6). Natural fibers could be an alternative for composites subjected to constant deformation. Kanking *et al.* [29] reported that NR/hybrid (silica+BFA) composite showed better compression performance than NR/silica. TESPT had no effect on compression set in the hybrid compound, while NBR/silica_{-TESPT} had slightly worse performance.

Hardness

The Shore A hardness of the NBR vulcanizates is shown in Figure-7. The incorporation of 25 phr of PSH had a significant effect on the hardness (p-value 0.002 Table-5). The hybrid compounds had a hardness of 77 Shore A, which was higher in 10 and 12 units compared to NBR/silica and NBR/silica_{-TESPT}. These results agree with Prukkaewkanjan *et al* [47] who reported an increase of 12



shore A units by adding 10 phr of PALF to 30 parts of carbon black in NBR composites. The addition of a rigid phase as VFs to the elastomer increases the hardness [28, 48, 49].

TESPT had no effect on hardness (Tables 5-6). Some studies show opposite behaviors of coupling agent respect to hardness. NR composites with TESPT exhibit higher hardness than the similar composites but without silane [26]. While Chandra *et al.* [30] observed a marginal reduction of hardness with the addition of TESPT in NR/silica composites, as a consequence of a plasticizing effect of silane residues [30].

CONCLUSIONS

NBR/hybrid composites showed higher hardness and similar performance in compression set and tear with respect to NBR/ silica composites. With respect to tensile strength, elongation at break and abrasion resistance, the NBR/hybrid showed a lower performance than NBR/silica, probably the large particle size of PSH and low interfacial adhesion PSH/NBR affected the performance of the hybrid compound. The direct addition of TESPT on the hybrid blend produced a significant improvement in the tensile and elongation properties of NBR/hybrid_{TESPT}, however its effect did not improve tear strength and abrasion resistance. It is likely that the presence of coarse particles of PSH limited the performance of the silane.

Finally, PSH is promising filler, it is recommended to use smaller particle size and mercerization. In situ addition of silane is a good option to develop rubber compounds, achieving a balance between mechanical performance and sustainability.

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