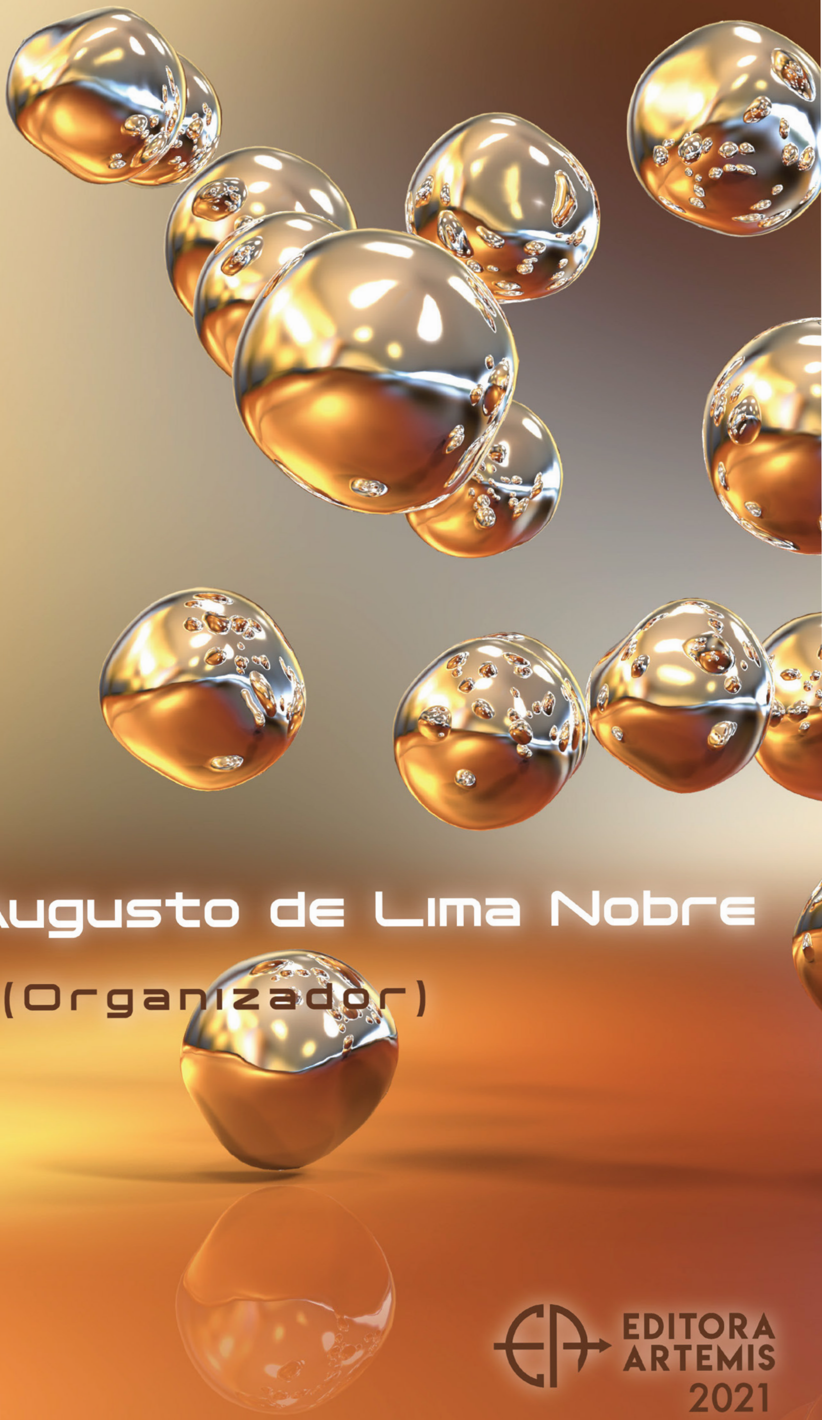
THE GREAT WORLD OF NANOTECHNOLOGY



Marcos Augusto de Lima Nobre

(Organizador)

VOL II

EDITORA ARTEMIS
2021

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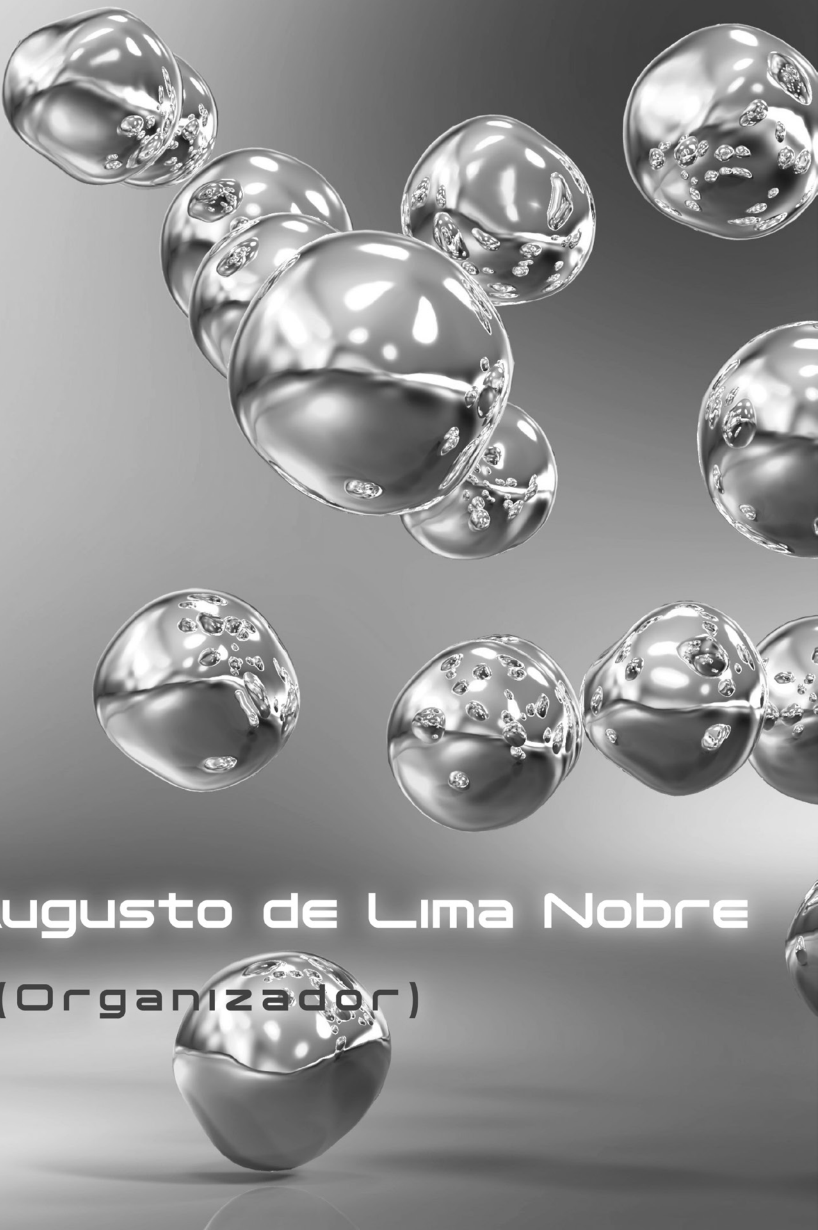

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PREFACE

The insertion of new and enhanced materials based on materials belonging to the Nano scale in the day-by-day has growth up in a silent way. In part, a number of works in the nanotechnology stemming of theoretical research using Density Functional Theory (DFT) and sophisticated simulation methods; another part is associated to the protected technologies associated to the military and patented nanomaterial and its process. In this sense, open access to recent aspects on the nanostructures application and properties can be reached in this book. Here, an interesting set of chapters gives opportunity of access texts that reach process and processing of nanostructures, applications of nanotechnology, advanced techniques to theoretical development. A broad set of nanostructures are here covered such as, nanocrystal, superficial nanograins, inner microstructures with nanograins, nanoaggregates, nanoshells, nanotubes, nanoflowers, nanoroad, nanosheets, Also, reveals new investigations areas as grainboundary of nanograins in ceramics and metals. A great number of software has been used as a tool of development of Science and Technologies for nanotechnology COMSOL Multiphysics 5.2. Phenomena and properties has been investigated by recent or classical techniques of materials characterization as Localized Surface Plasmon Resonance (LSPR), X-ray photoelectron spectroscopy (XPS), Field Emission Gun Scanning Electron Microscopy (FEG-SEM) with Energy Dispersive Spectroscopy (EDS), Raman Scattering Spectroscopy (RSS), X ray diffraction (XRD), ^{57}Fe Mössbauer spectroscopy, UV-vis spectroscopy, dynamic light scattering (DLS), Atomic Force Microscopy (AFM), and Field Emission Gun Scanning Electron Microscopy (FEG-SEM). In this sense, collections of spectra from Mössbauer spectroscopy, UV-vis spectroscopy and Infrared spectroscopy can be found. As a matter of fact, some chapter's item can be seemed as specific protocols for synthesis, preparations and measurements in the nanotechnology.

I hope you enjoy your reading.

Prof. Dr. Marcos Augusto Lima Nobre

TABLE OF CONTENTS

TABLE OF CONTENTS

CHAPTER 6

AMORPHOUS MICRO AND NANO SILICA EXTRACTED FROM RICE HUSKS AND OBTAINED BY ACIDIC PREHYDROLYSIS AND CALCINATION: PREPARATION ROUTE AND CHARACTERIZATION

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ABSTRACT: This chapter presents the characterization of three kinds of silicas produced by three different routes of preparation (PH, C and B) in order to replace traditional Commercial Silica (Z), widely used in the Industry of Elastomer. The PH Silica was obtained by acidic prehydrolysis of rice husks. The C and B Silicas are typical ashes of rice husks commercialized as amorphous silica of rice husks and Z Silica was obtained from quartz sand. The morphological assays identified morphologically different products due to the different routes of preparation. C and B Silicas presented well-defined and

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irregular grains, while PH and Z Silicas presented an agglomerate formation of micro and nano particles, as well as high area and surface porosity. From the analyzed material, the Z and PH Silicas were the ones, which provided higher potential for processing and dispersion because their surface area was smaller than 200 m^2/g and DOP absorption higher than 235 mL/100g. Thus, the results point to a satisfactory potential for the use of PH Silica as an option to replace commercial Z silica, in addition to the possibility of adding value and allowing an environmentally acceptable disposal of the abundant waste produced by the industry of rice processing.

KEYWORDS: Rice husk Silica. Micro and Nano Silica. Silica Morphology. Comparison among Silica and reuse of waste.

MICRO E NANO SÍLICA AMORFA EXTRAÍDA DA CASCA DE ARROZ E OBTIDA POR PRÉ-HIDRÓLISE ÁCIDA E CALCINAÇÃO: ROTA DE PREPARAÇÃO E CARACTERIZAÇÃO

RESUMO: O presente capítulo apresenta a caracterização de três tipos de sílicas produzidas por rotas de preparação diferentes (PH, C e B) com o objetivo de substituir a Sílica Comercial (Z) amplamente utilizada na indústria de elastômeros. A Sílica PH foi obtida por pré-hidrólise ácida da casca do arroz, as Sílicas C e B são típicas cinzas de casca de arroz comercializadas como sílicas amorfas da casca do arroz e a Sílica-Z é obtida da areia quartzítica. Os ensaios morfológicos evidenciaram produtos finais morfologicamente distintos devidos às diferentes rotas de preparação. Para as sílicas C e B foram gerados apresentaram grãos bem definidos e irregulares enquanto que nas sílicas PH e Z houve a formação de aglomerados de micro e nano partículas como alta área e porosidade superficiais, que proporcionaram melhor potencial de processabilidade e dispersão, por apresentarem a área superficial menor que 200 m^2/g e absorção de DOP maior que 235 mL/100g. Desta forma, os resultados apontam para um satisfatório potencial de utilização da Silica-PH como opção para substituição da sílica comercial Z, bem como para a possiblidade de agregar valor e permitir um descarte ambientalmente aceitável para os resíduos produzidos em abundância pela indústria de beneficiamento de arroz.

PALAVRAS-CHAVE: Sílica da casca do arroz. Micro e nano sílica. Morfologia da sílica. Comparação entre sílicas e reaproveitamento de resíduos.

MICRO Y NANO SÍLICE AMORFA EXTRAÍDA DE LA PIEL DE ARROZ Y OBTENIDA POR PREHIDROLISIS ÁCIDA Y CALCINACIÓN: RUTA DE PREPARACIÓN Y CARACTERIZACIÓN

RESUMEN: Este capítulo presenta la caracterización de tres tipos de sílices producidas por tres rutas diferentes de preparación (PH, C y B) para reemplazar la sílice comercial tradicional (Z), ampliamente utilizada en la industria del elastómero. La sílice PH se obtuvo por prehidrólisis ácida de cáscaras de arroz. Las sílices C y B son cenizas típicas de cáscaras de arroz comercializadas como sílice amorfa de cáscaras de arroz y la sílice Z se obtuvo de arena de cuarzo. Los ensayos morfológicos identificaron productos morfológicamente diferentes debido a las diferentes rutas de preparación. La sílice C y B presentó granos bien definidos e irregulares, mientras que las sílices PH y Z presentaron una formación de micro y nano partículas aglomeradas, así como una alta porosidad de área y superficie. Del material analizado, las sílices Z y PH fueron las que proporcionaron un mayor potencial para el procesamiento y la dispersión porque su área de superficie era menor que 200 m^2/g y la absorción DOP mayor que 235 ml/100g. Por lo tanto, los resultados apuntan para un potencial satisfactorio para el uso de sílice PH como una opción para reemplazar la sílice Z comercial, además de la posibilidad de agregar valor y permitir una eliminación ambientalmente aceptable de los abundantes desechos producidos por la industria del procesamiento del arroz.

PALABRAS CLAVE: Sílice de la piel de arroz. Micro y nano sílice. Morfología de sílice. Comparación entre sílice y reutilización de residuos.

1 INTRODUCTION

The growth of developing countries has tremendously increased the consumption of energy, material and food. The maintenance of the environment requires the reuse of all kinds of waste [solid, liquids, emissions, greenhouse gas (CO_2), nuclear]. The solution to these issues depends on interaction in the fields of energy, materials, food and environment; such interaction will be one of the main characteristics of the third millennium. Modern society must make a great effort to promote the rational reuse of the tailings created by industrial and agricultural processing, as well as the reuse of urban solid wastes, by transforming them into economically competitive energy together with other forms of energy. These materials must have optimized properties, always bearing in mind the environment in order to produce minimum pollution during the transformation processes [1,2].

In this context of environmental assets reuse which can be transformed into high added value material silica from rice husks (RHS) can be added as a pozzolanic material to cement to produce high performance concrete (HPC), with resistance from 90 to 120 MPa. The world RHS production has the potential to reach more than 29 million tons/year [3], which can be amplified 3.5 times if rice straw silica is exploited in a better way (10% silica and a collection rate equal to rice production). Taking into consideration that cement production is 3,300 million tons/year [4] and that the adding of 10% silica to high performance concrete (HPC 90 MPa) triplicates the resistance of simple concrete (SC 30 MPa), it can be concluded that rice straw and husk silica is enough to cater for all the demand of the civil construction market[2].

The production of micro and nano silica from the rice husk by the calcination process of the *in natura* husk has the following main process variables - temperature, time and combustion atmosphere. The treatment of inorganic contaminant removal is also evaluated [5]. Regarding temperature and the atmosphere of carbonization, a homogeneous distribution of nano-scale particles of silica can be obtained from the rice husk when it is burned at temperatures between 873 and 1073 K, in a pure oxygen

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[2] [(29 x 10^6 t of RHS/yr.d)/0.1)] x 3.5 times x 3 times higher resistance = 3.1 x 106 T of RHS/a

atmosphere [6]. Alternatively, micro and nano silica with a high surface area, which is essentially amorphous, can be obtained from rice husks burning at 973 K in air, since silica undergoes thermic treatment for 6 hours [7] or when burning is over, in fluidized bed boilers at temperatures lower than 800°C [8].

Amorphous Silica with a purity of 95% and an average size of 60 nm is obtained after the controlled burning of the rice husk in an atmosphere of highly purified oxygen [9,10]. In studies performed about the kinetic modeling of the pyrolysis and the effect of the treatment on rice husks with different acids (hydrochloric, sulfuric, phosphoric) concerning the purity of the silica which was obtained, it was observed that hydrochloric acid is the most effective when removing metals which are considered impurities [11]. Amorphous micro and nano silica with a purity of 99.66% was obtained using treatment with HCl 3% solution in v/v before and after carbonization for two hours in an argon atmosphere, followed by 1 hour in an oxygen atmosphere [12]. Even though the thermic route required to obtain the silica consists of simple technology, the product presents a great variety of properties due to the difficulties found when controlling the parameters of the process. In this context, the search for efficient routes of processing which are capable of modulating the final properties of the silica is worthy of note.

In this study, PH, C and B micro and nano silicas were proposed as preparation routes to be compared with commercial Z Silica obtained from quartz sand. The PH ilica was obtained from the rice husk acidic prehydrolysis while C and B Silicas are typical rice husk ashes, commercialized as amorphous micro and nano silica of rice husks for the rubber and cement industry. Such materials are aimed at adding technological value and at providing a way of disposing of industrial waste. The silicas were characterized morphologically, structurally, physically and chemically and the results showed that the studied Silicas present potential to replace Commercial Z Silica, depending on the requirement needed.

2 EXPERIMENTAL SECTION

2.1 PREPARATION OF THE SILICAS

In this work three silicas (PH, C and B) were prepared for comparison with Commercial Z-Silica. Z-Silica is widely used as a reinforcement filler in the Rubber Industry and it has a large consumer market. The description of the Silica preparation is presented as follows:

PH-Silica: Amorphous silica obtained by acidic prehydrolysis of rice husks with sulfuric acid in a solution of 2% m/m at approximately 170°C. After this treatment, the material is calcined at 800°C;

C-Silica: Silica from Corradini Farm (Rio Grande do Sul State), commercially called CCA-PLUS, obtained by calcination of raw rice husks at 500°C for approximately 1 hour, later it is ground and sifted. This process is widely used in Africa and Asia and there are many different suppliers;

B-Silica: Brazil Silica (Rio Grande do Sul State), commercially called Microsilica 500, obtained by calcination of raw rice husks at 900°C for approximately 1 hour, later it is ground and sifted; and

Z-Silica: Zeosil-125 Silica (RHODIA), commercial silica obtained by a reaction of quartz sand with sodium hydroxide in water and a precipitation with diluted sulfuric acid, later it is ground and sifted.

The high cost of chemical processes is the biggest limiting factor for a large scale application of this silica in elastomers, refractory materials and cement.

2.2 CHARACTERIZATION OF THE SILICAS

In order to evaluate the potentiality of the C, B and PH Silicas which were studied in this work as alternatives to Commercial Z Silica, a series of assays was proposed, the parameters of which are presented as follows:

Scanning Electron microscopy (SEM)

The images of Scanning electron microscopy of silica particles were obtained by using a JEOL JSM-820 microscopy, Quanta 200 model with a field emission gun (FEG). The images were taken on the sample surface.

Raman scattering spectroscopy (Raman)

The investigation of the molecular structure of the particles was carried out using a Raman scattering spectroscopy in a micro-Raman spectrophotometer, Renishaw, In-Via model in the observation region between 1800 and 1200 cm^{-1} . The exposure time of the sample to the laser was 10s, 1 accumulation, laser with wavelength equals to 785 nm and used at 100% of its power.

Oil Absorption Number

The assay of oil absorption is used to measure the porosity of the product and consists of the incorporation of the Dioctyl Phthalate Oil (DOP) (Specification: analytic purity, minimum title of 99% in ester) to the silica sample, until a well-defined absorption point is reached. DOP is added progressively in order to obtain a small cylinder of silica and DOP. As for the silica particles, the DOP index was estimated according to DOP equation (mL/100g) = {[used DOP volume (mL)]/sample mass (g)]}x100.

Specific Surface (BET)

The measuring of the surface area of silica particles was carried out using a Nova 10000 model quantachrome instrument, and by the Brunauer-Emmer-Teller method (BET) founded in adsorption of N_2 by the sample surface.

Particle size distribution Analysis

For particle size analysis, Cilas equipment, model 1180L, was utilized to measure the average size of the particles and granulometric distribution by laser diffraction. For this assay, 1.00 g of sample was used.

Chemical Silica Analysis

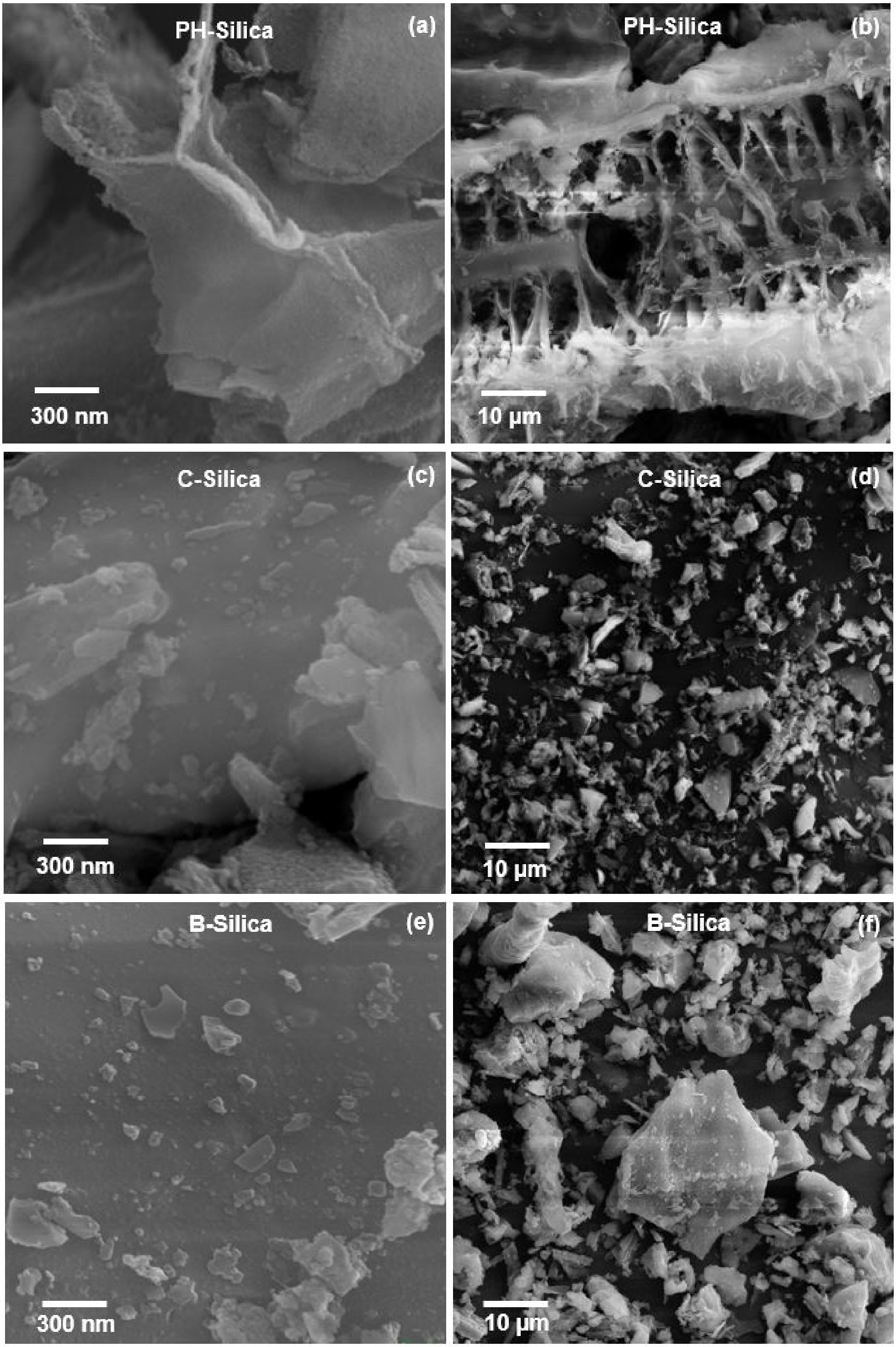
The chemical analysis of the silica was made by x-ray fluorescence spectometry, in a Shimadzu spectrometer, model XRF1800, Rh tube. The samples used in the assay were weighted, 1.00g and patched using 50% in mass of boric-acid.

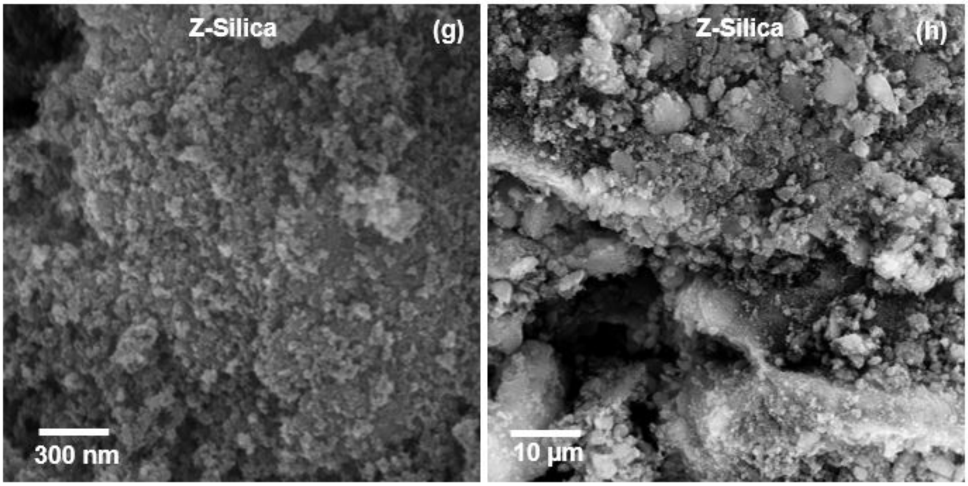
3 RESULTS AND DISCUSSIONS

3.1 MORPHOLOGICAL ASSAY FOR THE SILICAS

Electronic Microscopy techniques are typically used to evaluate the surface structure of samples due to the excellent relation resolution/preparation of the sample. Figure 1 shows SEM images of the surface of the micro and nano particles of PH-Silica [(a) and (b)], C-Silica [(c) and (d)], B-Silica [(e) and (f)] e Z-Silica [(g) e (h)]. The amplification used was equal to 25,000 and 1,000 times. As can be observed in Fig. 1, in all four types of primary particles, the geometry is approximately non spherical due to the growing mechanism of the particle (nucleation) predominant in ceramic materials and to the principle of surface energy minimization. Therefore, if the thermal energy source were maintained, an increasing in the grain size via the coalescence phenomenon would be expected, together with a reduction in the numbers of grains, a reduction in the grain boundary area and, therefore, the surface energy would decrease. The use of different routes for the silica preparation generated some final micro and nano materials, which were morphologically different. In the case of C and B silicas, very-well defined grains were observed, although somewhat irregular, with low surface porosity. In the case of PH and Z silicas, the formation of an agglomerating of particles was identified, which is typical of a chemical route synthesis, as well as high area and surface porosity. Different morphological characteristics provide different surface properties, such as surface energy, zeta potential, interaction with radiation, different coefficients of thermal diffusion and different capability of chemical absorption, besides the capability of significantly altering the mechanical properties of polymeric matrices, such as synthetic and natural rubber [13]. For both observed structures, their dimensions are in the micrometer and nanometer scales and they are coherent with the diameter of particles previously reported in scientific literature [14,15].

Figure 1. Scanning electron microscopy images from the surface of the particles of PH-Silica [(a) and (b)], C-Silica [(c) and (d)], B-Silica [(e) and (f)] and Z-Silica [(g) and (h)]. The magnifications utilized were equal to 25.000 and 1.000 times.

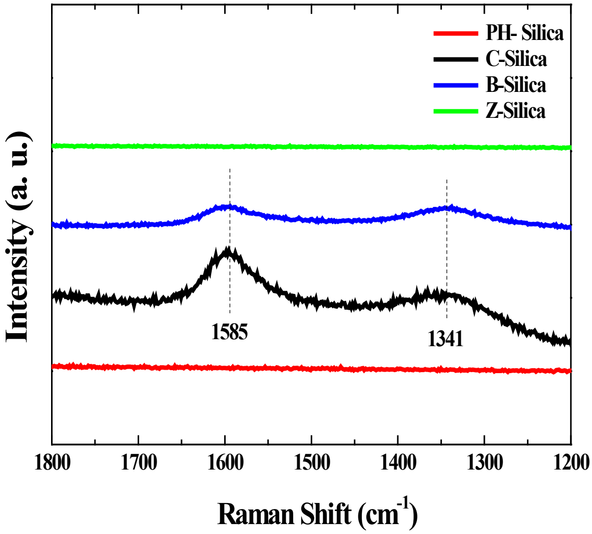




3.2 STRUCTURAL CHARACTERIZATION OF THE SILICAS

Low cost of the equipment, high accuracy results, low necessity of sample preparation, wide range of usage and easy handling. The Raman spectra with a wavelength between 1800 and 1200 cm^{-1} for PH-Silica, C-Silica, B-Silica and Z-Silica particles are shown in Figure 2. The Raman spectrum for silica particles presents a typical profile of amorphous material due to the non-resolution of the peaks in the region of low wavenumber. The nonresolution of peaks is also related to the fluorescence phenomenon, due to the presence of organic matter, originated from chemical synthesis processing, especially carbonic groups, such as those identified through chemical analysis shown in Table 3. For B and C silica samples, two low resolution and intensity bands were identified, characterizing the formation of a short-range ordering state. Such observation corroborates the microscopy images in Fig 1, in which the difference between the PH and Z silica morphology is clear, with agglomerates of particles, and C and B Silicas, with well-defined micro and nano grains. Both bands or superposition of bands with maxima in 1341 and 1585 cm^{-1}, are associated to vibrations of carbon-carbon bond and carbon-silica, as studied by T. Narushima *et al* [16]. From a morphological point of view, Fig 1, and structure, Fig. 2, The PH Silica resembles commercial Z Silica, reflecting the potential for the use of the silicas proposed in this work.

Figure 2. Raman spectra with wavelength between 1800 and 1200 cm-1 at room temperature for PH-Silica, C-Silica, B-Silica and Z-Silica micro and nano particles. Utilized laser: λ = 514 nm and 10s of sample exposition.



3.3 PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical properties of the materials reflect the characteristic behavior of the material when submitted to physical stimuli or when in contact with other substances. Such properties determine the range of technological uses of the material and can be modulated to improve the relation property/application. Table 1 lists the physical and chemical parameters pH, specific surface area and oil adsorption (DOP) of the PH-Silica, CSilica, B-Silica and Z-Silica. According to the data listed in Tab. 1, as expected and desired, the PH, C and Z silicas presented a neutral character, around 7, while B-Silica presented a basic character, pH = 10.4. It is suggested that the basic character of the B-Silica sample is a result of excess organic matter which originated from thermochemical processing, mostly in the case of magnesia (MgO), which is well known for its basic pH. From the perspective of material processing and the use of micro and nano silica as a burden in polymeric matrices, it is desirable to have pH values close to 7, neutral in character, in order to avoid interference in the curing process or in the matrix polymer chain. As for the surface area, estimated in this work via BET, values higher than 100 m^2/g are currently considered satisfactory for a good dispersion in the polymer matrix, besides assuring an adequate surface activity to interact with other materials. Out of the materials which were prepared, only the B-Silica samples presented low values of surface area, which were possibly associated to micrometric scale and, predominantly, to the smallest amorphous character of the material as identified by SEM images. Once the oil absorption (DOP) assays had reflected the combination between the surface area parameters, surface porosity and particle size variation, the B-Silica sample presented the lowest value of oil absorption (DOP), due to its low area and porosity surface, see Fig. 1 (f), while the Z-Silica sample presented the highest value of the same parameter, resulting mainly from high area and porosity surface, see Fig. 1 (h). According to A. Blume *et al* [17], a good estimative of the silica processability and dispersion in polymer matrix results from the combination of the surface area and the oil absorption (DOP). According to this correlation, silicas with good processability or dispersion are the ones which present a surface area which is smaller than 200 m^2 /g and oil absorption (DOP) which is higher than 235 mL/100g. It is worth emphasizing that it would be possible to adjust the processing parameters of the PH-Silica by introducing grinding and micronizing stages in order to adjust its surface characteristics to those of Z-Silica.

Table 1. List of physical and chemical parameters pH, BET and DOP absorption for PH-Silica, C-Silica, B-Silica and Z-Silica particles.

Samples	**Physical and Chemical Properties**		
	pH	**Specific Surface Area (m^2/g)**	**DOP Absorption (mL/100g)**
PH-Silica	6.9	94.2	112
C-Silica	7.5	112.0	84
B-Silica	10.4	25.1	66
Z-Silica	7.0	120.4	250

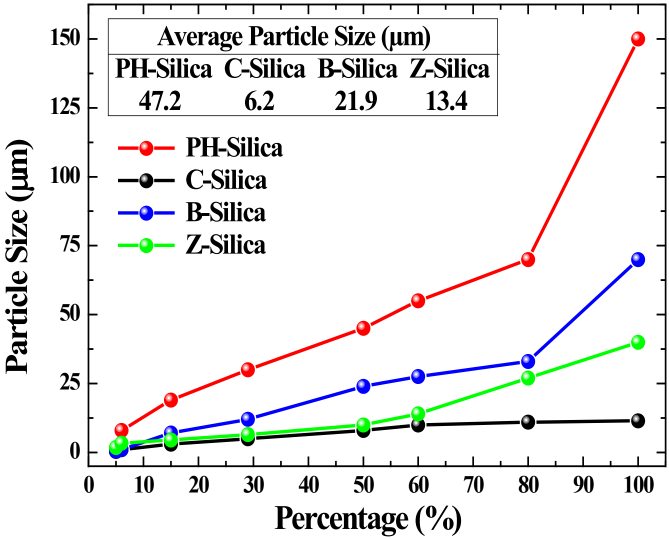
The grain size analysis of the particulate materials reports the distribution and the percentage frequency of dimensional occurrence of the grains or agglomerates. Thus, it is possible to estimate the interaction profile of the particles and particle/matrix, reactivity and average size of the particulate material. Table 2 lists the grain size distribution (size of particles and aggregates) whereas Figure 3 shows the evolution of the granulometry to the PH-Silica, C-Silica, B-Silica and Z-Silica particles. In Fig. 3 the average particle size of each of the samples studied are listed. Once Z-Silica had become the commercial material with the desired set of properties, it was used as reference and comparison material. It was observed that the PH-Silica presents an average particle diameter which is bigger than Z-Silica, see Tab. 2 and Fig. 3. This fact indicates that, if this kind of burden were inserted into a polymer matrix, such as SBR 1502 rubber, inferior mechanical properties would be expected when compared with composites of Z-Silica. This is partly due to the lesser availability of the silanol groups to interact with the polymer matrix. When comparing the size of the particles, it is seen that the PH-Silica particle is 3.5 times bigger than the Z-Silica particle, demonstrating that in order to become similar to the PH-Silica properties, it would be necessary to insert micronizing stages in the preparation process of the PH-Silica. As for value adding, it is considered that the insertion of micronizing stages presents a favorable benefit-cost ratio, once it is possible to convert rice husk waste into particulate burden in a well-defined consumer market.

Table 2. Grain size distribution (particle and aggregate size) for PH-Silica, C-Silica, B-Silica and Z-Silica particles.

	%	**Samples**			
		PH-Silica	**C-Silica**	**B-Silica**	**Z-Silica**
Particle Size Distribution: Particle size (µm) for each percentage value (%)*	**0.5**	0.5	0.4	0.5	1.8
	6	8.0	1.0	1.0	3.4
	15	19.0	3.0	7.0	4.5
	29	30.0	5.0	12.0	6.5
	50	45.0	8.0	24.0	10.0
	60	55.0	10.0	27.5	14.0
	80	70.0	11.0	33.0	27.0
	100	150.0	11.5	70.0	40.0

* Example: 50% of the PH-Silica sample has particle size up to 45.0 µm.
80% of the Z-Silica sample has particle size up to 27.0 µm.

Figure 3. Evaluation of grain size for PH-Silica, C-Silica, B-Silica e Z-Silica particles.



The chemical analysis of the materials allows the chemical species present in the samples to be identified, besides establishing the relative quantity of each species. Table 3 shows the chemical composition of the PH-Silica, C-Silica, B-Silica and Z-Silica. Regarding the components from a quantitative point of view, it is possible to observe that the silicas display very different compositions, mainly due to the level of SiO_2. PH and Z silicas present high levels of SiO_2, which indicate the similarity between them, while the amorphous silica B and C display a 20% lower quantity of SiO_2. Besides, they are rich in different metals, which, when in oxide form interact, with SiO_2 and reduce the level of silanol. The fact that the B and C Silicas present considerable levels of carbon is also noteworthy, 18.55%w/w and 16.27%w/w, respectively, probably because of incomplete combustion of the rice husks organic fraction, but which can also bring functionality to these materials regarding their electrical and thermal conductivity. When comparing PH and Z Silicas, it is observed that the PH-Silica presents low levels of trace elements (Ca, Fe, Al, S, P and K), while Z-Silica is 100% SiO_2. It is expected that the presence of trace elements in particulate burdens will provide a poorer mechanical performance of the composite when facing the properties of composites which are prepared with pure burdens.

Table 3. Chemical composition of PH-Silica, C-Silica, B-Silica and Z-Silica particles.

Compounds present in samples of Silica	**Concentration (%w/w)**			
	PH-Silica	**C-Silica**	**B-Silica**	**Z-Silica**
SiO_2	99.1	80	80	100
CaO	0.3	0.5	0.5	ND
MgO	0	0.8	0.28	ND
Fe_2O_3	0.06	ND	0.1	ND
Al_2O_3	0.18	0.15	0.65	ND
Na_2O	ND*	ND	ND	ND
K_2O	0.06	ND	0.88	ND
TiO_2	ND	ND	0.02	ND
MnO	ND	ND	0.2	ND
SO_3	0.22	ND	0.3	ND
P_2O_5	0.08	ND	0.8	ND
Carbon	ND	18.55	16.27	ND
Total	**100**	**100**	**100**	**100**
Water insoluble salts	ND	ND	1.03	1.2
Humidity	2.0	1.0	2.3	5.0

* ND = Not Detected.

3.4 SPECIFIC DENSITY OF SILANOL GROUPS

Silanol groups are derived from silanes in which a hydroxyl group replaces a hydrogen, $Si_nH_{(2n+1)}OH$, where n is the number of atoms of Si. Silanol groups can be of isolated, vicinal and germinal types. The germinal type presents the most reactive surface of the three [18]. According to L. T. Zhuravlev [19] and C. Airoldi *et al* [20], the physical constant which relates the quantity of hydroxyl groups per molecule area can be considered equal to 5.0 OH/nm^2 in all kinds of silica. Taking this into account, a good estimative for the density of silanol groups in mol.OH/g can be obtained using the surface area of the silica in m^2/g and the constant to the above cited silicas (5.0 OH/nm^2 x10^{18} nm^2/m^2 = 5.0x10^{18} OH/m^2), as listed in Table 4. When analyzing the data of Tab. 4, it is verified that, in the second column (nr. of mol OH/g *with* carbon) for B and C Silicas, the number of OH/g moles has been calculated considering the surface of "silica + carbon", once B and C silicas contain about 17-18% of carbon weight, see Tab. 3. However, the silanol groups are only found on the silica surface. For this reason, the number of OH/g moles without carbon (last column) was estimated. Probably the K_2O, Na_2O, CaO, and MgO impurities decreased the quantity of silanol and the other impurities were considered inert.

Table 4. Specific density of silanol groups for PH-Silica, C-Silica, B-Silica and Z-Silica particles.

Sílicas	Specific Surface Area (m^2/g)	no. mol OH/g com carbono	no. mol OH/g sem carbono
PH-Silica	94.2	7.82x10^{-4}	7.82x 10^{-4}
C-Silica	112.0	9.29x10^{-4}	7.44x10^{-4}
B-Silica	25.1	2.08x10^{-4}	1.67x10^{-4}
Z-Silica	120.4	9.99x10^{-4}	9.99x10^{-4}

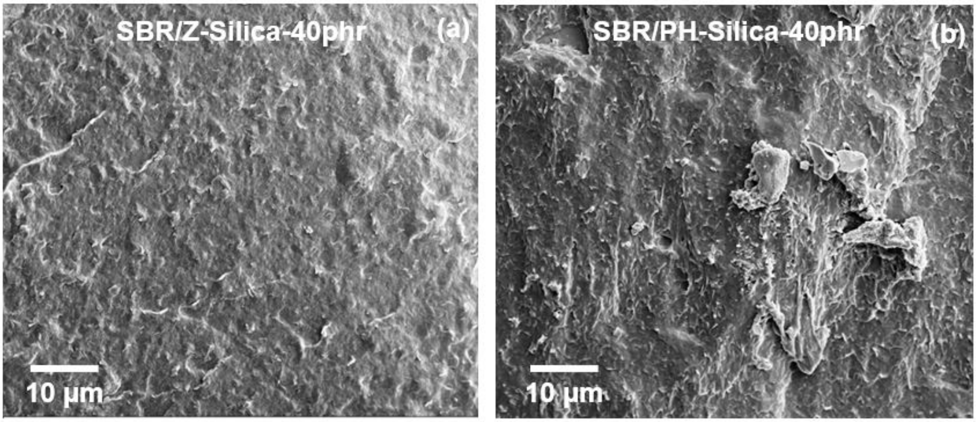
3.5 POTENTIAL APPLICATION TO THE PH-SILICA

Aiming to evaluate the potential utilization of PH-Silica as a possible replacement for commercial silica, Z-Silica, in styrene-butadiene rubber (SBR) formulation, exploratory tests utilizing composites based on SBR rubber loaded with 40 phr (parts per hundred rubber) of Z-Silica (SBR/Z-Silica-40phr) or of PH-Silica (SBR/PH-Silica-40phr) were carried out. Figure 4 and Table 5 respectively, show images of scanning electronic microscopy (SEM) of micro and nano composites and some main mechanical parameters for both samples. As can be seen in the SEM images, a satisfactory dispersion could be observed for both composites, as well as, a good coupling between particles and polymeric matrix with a low quantity of remnant silica particles with a diameter size of 3 μm, almost 5 times lower than the initial diameter size of silica (13.4 μm), indicating a deagglomeration dispensation due to the mechanical processing of the composites [21]. From a mechanical point of view, differences of more than 20% were not obtained, with the exception of the tensile strength at break and elongation at break. However, it should be noted that the materials are not strained to breaking point in normal applications and the lowering of breaking stress does not undermine the material in comparison to its enhancement in elastic properties. Thus, from the mechanical and morphological points of view, the PH-Silica particles exhibit a potential to replace Z-Silica (commercial) particles in the SBR rubber industry. A more detailed study concerning the mechanical and morphological properties will be presented in a future publication.

Table 5. Exploratory testing to evaluate the potencial of replacement of commercial silica to PH-Silica in samples of styrene-butadiene rubber (SBR). List of mechanical parameters comparing samples of SBR rubber loaded with 40 phr of Z-Silica and PH-Silica.

Parameter	**Mechanical Properties**	
	SBR/Z-Silica-40phr	**SBR/PH-Silica-40phr**
Hardness Shore A	61	53
Permanent Deformation (% for 22h/100 °C)	21.8±3.2	29.7±1.5
Abrasion Index (mm^3/40m)	66.4±10.5	101.4±15.5
Mooney Viscosity (ML 1+4) 100°C	112.8	95.2
Tensile Strength (MPa) at 100%	2.0±0.3	2.1±0.1
Tensile Strength (MPa) at 300%	7.8±0.7	5.3±0.1
Tensile Strength at break (MPa)	15.1±0.1	3.1±0.1
Elongation at break (%)	870.9±10.5	497.7±41.5

Figure 4. Exploratory testing to evaluate the potencial of replacement of commercial silica to PH-Silica in samples of styrene-butadiene rubber (SBR). (a) Images of SEM for SBR rubber loaded with 40 phr of Z-Silica (SBR/Z-Silica-40phr) and (b) images of SEM for SBR rubber loaded with 40 phr of PH-Silica (SBR/PH-Silica-40phr).



4 CONCLUSIONS

The thermochemical route (acidic prehydrolysis followed by calcination at 800°C) for production of rice husk micro and nano silica showed that it is possible to obtain material with morphological, physical and chemical characteristics which are capable of replacing commercial silica for application in elastomers. The results of the characterizations obtained indicate micronizing as a mandatory stage in order for the PH Silica to have a similar performance to Z-Silica. The initial objective of transforming a highly pollutant environment liability into an additive in the rubber industry was achieved, making large scale supply possible in a competitive cost in comparison with the quartz sand silica. In addition to obtaining PH-Silica, it is possible to obtain an amorphous silica for a cement application and also generates electric energy in an integrated industrial plant using rice husks as a raw material.

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INDEX

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