



Polímeros: Ciência e Tecnologia

ISSN: 0104-1428

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Brasil

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Polímeros: Ciência e Tecnologia, vol. 24, núm. 6, 2014, pp. 646-653

Associação Brasileira de Polímeros

São Paulo, Brasil

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Sugarcane Bagasse Ash: New Filler to Natural Rubber Composite

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Abstract: Waste recycling has been the subject of numerous scientific researches regarding the environmental care. This paper reports the redirecting of sugarcane bagasse ash (SBA) as new filler to natural rubber (NR/SBA). The NR/SBA composites were prepared using an opened cylinder mixer to incorporate the vulcanization agents and different proportions of residue (SBA). The ash contains about 70-90% of inorganic compounds, with silica (SiO_2) being the main compound. The SBA incorporation improved the mechanical properties of the vulcanized rubber. Based on these results, a new use is proposed for the agro-industry organic waste to be implemented in the rubber vulcanization process, aimed at improving the rubber physical properties as well as decreasing the prices of natural rubber composites.

Keywords: *Sugarcane bagasse ash, natural rubber, vulcanization, recycling; biomass.*

Introduction

Waste recycling has become a very important topic of research as result of both environmental improvement and generation of new composites materials. The Kyoto Protocol (1997) proposed the emission reduction of greenhouse gases by 5.2% compared to the concentration levels in 1990^[1]. The aim is the production of biofuel, mainly from sugarcane, as an alternative source to replace, even partially, fossil fuels and thereby reduce greenhouse gas emissions as well as enable the cogeneration of electric energy from waste (biomass) production.

Approximately 660 Mton of sugarcane could generate a total of 28,500 million liters of alcohol, designed to produce 45.4% of sugar and 54.6% of alcohol^[2]. This production would be equivalent to 160 Mton of sugarcane bagasse produced. Basically the composition of sugarcane bagasse is cellulose (41.0-55.0 wt%), hemicellulose (20.0-27.5 wt%), lignin (18.0-26.3 wt%) and others (~7.0 wt%) attributed to inorganic materials^[3]. Part of the sugarcane bagasse generated is burned and yields the power to companies' sustainability.

Currently, about to 50% of energy production in Brazil comes from renewable sources, being 18.8% relative to sugarcane products (5% from burn the sugarcane biomass)^[3]. However, through this cogeneration power gets a new residue, ash on estimated amounts for the current crop as being around 3.84 Mton.

Besides sugarcane bagasse is used for generation of energy, it can be considered for other applications, such as in studies related to cellulose^[4] or extraction of lignin from biomass^[5]. In addition, the sugarcane bagasse ash is used as raw material for obtaining ceramic materials^[6], and for the partial replacement of Portland cement to produce mortars and concretes^[7].

Another material widely used in industry is the natural rubber latex. It is a natural, biocompatible and flexible

polymer obtained mainly from the *Hevea brasiliensis* tree. In general, rubbers are benefited by vulcanization processes which consist of the crosslink of the polymer chains improving mainly the mechanical properties of the compound^[8,9].

Currently, the rubber has been of great interest of study as result of the possibility of composites preparation as a new approach to technology development^[10,11] which may contain organic compounds such Defatted Soy Flour^[12], or carbon black^[13,14] as both reinforce and conductive agents.

In this study we propose a new use for waste produced in the processes of sugarcane industry, using the ash from sugarcane bagasse burn (residue) as a reinforcing agent in the vulcanization process of natural rubber. It is known that the use of commercial silica could increase the manufacture cost due to its high market value. However, this cost could be reduced using silica obtained from organic waste. A Similar study recently reported in the literature describes methods for obtaining silica from rice hull ash (residue production)^[15-17], oilshare residue^[18], and the use of organoclay as a substituent of silica (fillers) in rubber composites^[19].

Materials

The natural rubber used in this project was the Brazilian *crepe claro* from DLP industry. The residue from burning sugarcane bagasse was obtained from the beneficiation process carried out in Alto Alegre industry in the city of Santo Inácio. The SBA particles were dried, annealed at 80 °C, during 24 hours as well as sieved using 325 mesh (particles sizes smaller or equal than 45 microns). Microscope evaluation of the SBA particles (Figure 1) shows irregular shapes as well as sizes varying from 2 to 40 μm . The irregular shapes make the particles more

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susceptible to the interaction with the natural rubber, i.e. improving the reinforcement by interfacial interactions (filler-polymer).

The materials used in vulcanization process are: stearic acid, zinc oxide, CBS (N-cyclohexyl-2-benzothiazolesulphenamide) and sulfur from VETEC QUÍMICA FINA LTDA.). Carbon black (N-330) with a surface area 80 m²/g was acquired from Fragon Produtos para Industria de Borrachas.

Experimental

The composites were produced by mixing the natural rubber (NR) and sugarcane bagasse ash (SBA), NR/SBA. It was prepared five different composites varying the SBA amount from 10 to 50 phr (*per hundred of rubber*). The pure gum (rubber vulcanized) was used as standard to compare the results obtained from the composites produced.

For the production of composites, natural rubber and sugarcane bagasse ash were mixed in an open chamber mixer (Makintec brand - model 379 m) during 20 min. at 70 °C and friction 1.0:1.25 as well as vulcanizing agents were subsequently added to the mixture.

The proportions of materials (reagents) used for composite preparation is respectively, 100.0 phr of natural rubber, 3.0 phr of stearic Acid, 3.0 phr of zinc oxide, from 0 to 50.0 phr of sugarcane bagasse ash, 3.0 phr of sulfur and 1.5 phr of N-cyclohexyl-2-benzothiazolesulphenamide (CBS). The amount of 50.0 phr of carbon black (N-300) was used as comparative composite.

After that, the composites were thermally pressed at 5 tons and 150 °C during its respective optimum vulcanizing time (t_{90}), which was obtained by rheometry technique.

Rheometry Parameters

The natural rubber composites were analyzed on an oscillating disk rheometer at 150 °C, with 1° arc, according to ASTM D-2084. Based on the rheometric curves, it was determined the minimum torque (ML), maximum torque (MH), pre-curing time (T1) or scorch and optimum vulcanizing time (t_{90}), i.e. the time required for the formation of 90% of cross-links in the samples. The relation between the sulfur and the accelerator used define the vulcanization system as the conventional type. This system gives the material excellent mechanical properties, such as fatigue resistance, abrasion, deformation and scratch^[20].

Characterization

The evaluation of the morphological properties of the SBA particles was carried out using a scanning electronic microscope Carls Zeiss model EVO LS15, back-scattering detector, high vacuum, potential of 20 kV. The samples were previously covered with gold thin film by Sputtering device Quorum model Q 150R ES.

The stress-strain tests were performed in samples shapes type C using an EMIC test machine model DL 2000, according to ASTM D-412.

The abrasion resistance was evaluated using rotating cylindrical drum device, Abrasion machine - MaqTest. The cylinder shall have a diameter of 150 ± 0.2 mm and a length around 500 mm which rotating at a frequency of 40 ± 1 min⁻¹. The samples were prepared according ASTM D 5963-97 – method A, five replications for each composite (amounts of SBA) implementing cylindrical samples with diameters of 16.0 ± 0.2 mm and thickness of 6.0 mm. The tests were carried out along 40 m (friction route) under applied force of 5.0 N.

The thermogravimetry (TG) analyses were carried out using a Netzsch model 209. About 15.0 mg of sample mass were deposited in an alumina (Al₂O₃) crucible, and pure nitrogen gas (N₂) was used as carrier gas (15 mL/min). The heating rate was 10 °C/min and the temperature between ~25 and 900 °C.

The differential scanning calorimetry (DSC) analyses were performed on Netzsch model 214 Phoenix. 5.0 mg of each sample was deposited in an aluminum crucible with a heating rate of 10 °C/min. The temperature ranged from –120 to 500 °C in N₂ atmosphere with flow of 15 mL/min.

For the dynamical mechanical analysis of the composites, it was used NETZSCH DMA 242C interface TASC 414/3A and controller 242. The tests conditions were 5.0 Hz frequency, temperature from –120 to 150 °C and heating rate of 5 °C/min. The cooling process was carried out in N₂ atmosphere and the maximum deformation was 0.025% with maximum amplitude of 60 m. The maximum dynamic strength was 5.0 N and static force 1.5 N with dynamic force applied. The average dimensions of the samples were 6.0 mm length, 3.0 mm width and 1.5 mm thickness. All characterizations were performed after vulcanization process (thermally pressed) implemented to NR/SBA composites.

Results e Discussion

The parameters obtained from the rheometrics tests (Table 1) showed that when the amount of SBA increases, the values of the minimum (ML) and maximum (MH) torque also increases, while the pre-cure times (scorch) and the t_{90} were reduced. The increase of the minimum torque is directly related to the increasing of viscosity by the addition of the filler. The viscosity increases according to the reinforcing character of the filler. The increase of the maximum torque is directly related to the curing degree, i.e. the number of cross-links formed during the vulcanization process. The relation between the maximum and minimum torque (ΔM) define the degree of reinforcement from the filler incorporation^[21] which is increasing in terms of the amount of SBA particles (0-40 phr) incorporated on the composites. Moreover, when incorporated the amount of 50 phr of SBA particles decrease the rate of mechanical reinforcement. Irregularities from the surface of the SBA particles (Figure 1) make it more susceptible to the formation of the structural agglomeration decreasing contribution from fillers to reinforcement the polymer.

The reinforcement can be an indication of the interfacial interactions between the waste particles and the elastomeric

matrix. This interaction restricts the molecular motion of the polymer chains, which contributes to the torque increase although these interactions are not considered cross-links^[22].

It was verified the reversion of the vulcanization process for all composites which occurs due the chemical constituents of the vulcanized rubber generate, after long time procedures, the polymeric chain scission, related to the decrease on the maximum torque.

Thermogravimetric analyses (TG) were carried out for all NR/SBA composites and it is presented in Figure 2. A weight loss of 5% is observed around 100 °C is attributed to the release of water molecules or volatile compounds present in the composite. The second thermal event, at 350 °C, corresponds to the degradation of the polymer structure which is broadly discussed in the literature^[23,24]. The degradation process starts with the polymer chain scission and the formation cross-linking bonds, which generates shorter segments with the terminal radicals. The

cross-linking occurs simultaneously with the chain scission until it is all destroyed, around 400 °C.

The main difference in thermogravimetry curves is related to amount of residue which is directly proportional to the ratio of SBA insert on composites (final mass percentage from 3 to 30%, increased the amount of ash inserted in composites, from 0 to 50 phr, respectively.). Teixeira et. al.^[3] studied the SBA residue from sugarcane bagasse burn, classifying that the ash contains SiO₂ as the major inorganic component as well as Al₂O₃, Fe₂O₃, K₂O, CaO and TiO₂ among the minor components which is attributed to the main composition obtained from TG residual mass. EDS analysis coupled to the microscopy (Table 2) corroborate to the inorganic components indentified by Teixeira S.R. showing Al, Ca, K, Si as well as the increase on the oxygen compositions. The sulfur and zinc is associated to the vulcanization.

Figure 3 shows the differential scanning calorimetry (DSC) results of the NR/SBA composites. It was not

Table 1. Rheometric parameters obtained from the oscillating disk rheometer at 150 °C and 1° arc. (non vulcanized compounds).

Sample	Rheometric Parameters				
	M _L (lb.in)	M _H (lb.in)	ΔM (lb.in)	T _{sl} (min.)	T ₉₀ (min.)
NR _{pure}	0.70	27.90	27.20	2.6	3.5
NR _{SBA} (10 phr)	1.20	29.50	28.30	2.4	3.2
NR _{SBA} (20 phr)	1.50	34.50	33.00	2.3	3.2
NR _{SBA} (30 phr)	1.40	35.10	33.70	2.2	3.0
NR _{SBA} (40 phr)	2.10	35.80	33.70	2.9	3.0
NR _{SBA} (50 phr)	2.00	38.50	36.50	1.8	2.9
NR _{CB} (50 phr)	2.10	42.00	39.90	2.2	3.5

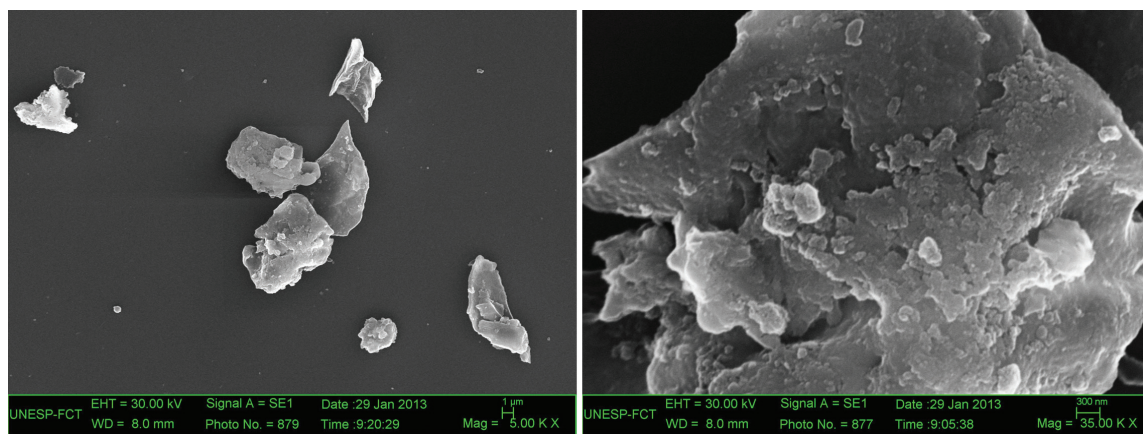


Figure 1. Scanning electronic microscope (SEM) images from sugar bagasse ash (SBA) particles.

Table 2. Chemical elements present on the surface of the composites evaluating by EDS spectroscopy.

Element	Natural rubber (Weight %)	Composite NR/SBA (50 phr) (Weight %)
Al	0.00	2.89
Ca	0.00	4.64
F	0.00	2.05
K	0.69	2.41
Mg	0.00	3.35
O	49.69	47.65
S	25.92	15.79
Si	0.00	9.68
Zn	23.69	11.54

observed significantly alteration in the glass transition temperature (T_g) (average on -58°C) (Table 3), *i.e.* notice only changes on materials heat capacity without alter the enthalpies ($H = 0$), related to the incorporation of SBA residue into the natural rubber. In this case, three parameters had been considerate: The natural polymeric restrict from vitreous state, the crosslink generation attributed to the vulcanization process and the interaction fillers-polymer.

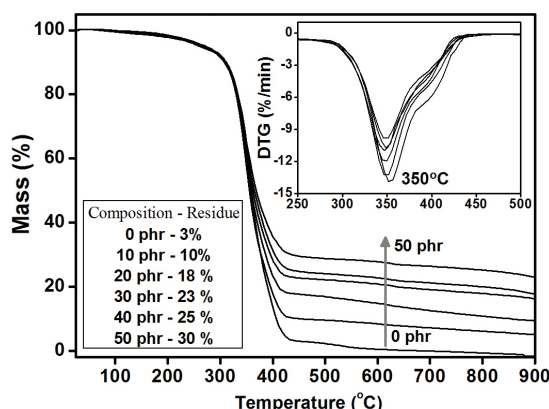


Figure 2. TG analyses of the NR/SBA composites prepared using 0, 10, 20, 30, 40 and 50 phr of SBA from room temperature to 900 °C in N_2 atmosphere. DTG (in set).

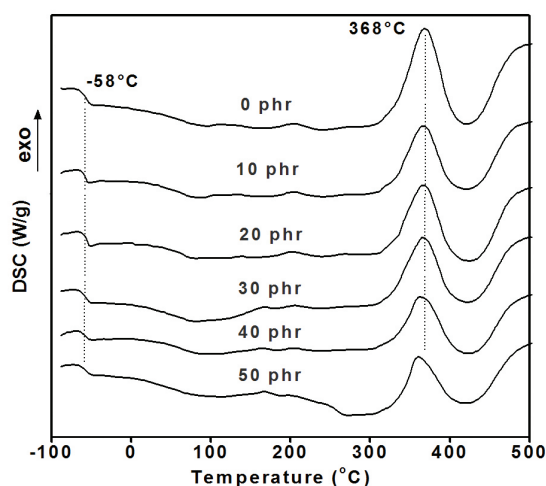


Figure 3. DSC analyses of the composites NR/SBA prepared using 0, 10, 20, 30, 40 and 50 phr of SBA from -100 to 500°C in N_2 atmosphere.

Table 3. T_g values obtained from dynamic mechanical analysis (DMA) for the composites of natural rubber with different amount of sugar bagasse ash (SBA).

Samples	DMA Analysis	DSC Analysis
	T_g ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)
NR _{pure}	-45.5	-58.7
NR _{SBA} (10 phr)	-45.5	-58.9
NR _{SBA} (20 phr)	-42.8	-57.7
NR _{SBA} (30 phr)	-44.4	-58.8
NR _{SBA} (40 phr)	-46.0	-58.5
NR _{SBA} (50 phr)	-42.9	-59.0

The value measured is lower than reported in the literature (-65°C)^[25] attributed to the vulcanization process. At 368°C observed the process of degradation of the polymeric chain, evident by exothermic peak, which can be equally related to the mass loss observed on thermogravimetric curves previously discussed (around 350°C).

Thermodynamic studies carried out using dynamical mechanical analysis (DMA) technique is presented in

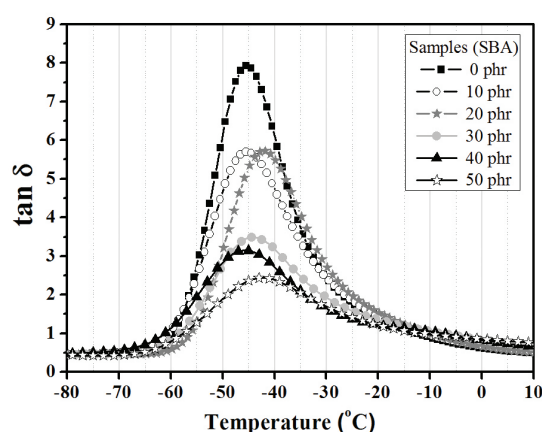


Figure 4. Studies of Tan δ curves obtained by DMA analyses of the composites NR/SBA prepared using 0, 10, 20, 30, 40 and 50 phr of SBA from -80 to 500°C in N_2 atmosphere.

Table 4. Resistance to abrasion of vulcanized rubber, composites with SBA and carbon black N330.

Samples	Abrasion resistance
	Abrasion loss ($\text{mm}^3 / 40 \text{ m}$)
NR _{pure}	64.50 ± 1.33
NR _{SBA} (10 phr)	68.04 ± 1.29
NR _{SBA} (20 phr)	76.34 ± 0.86
NR _{SBA} (30 phr)	83.49 ± 0.90
NR _{SBA} (40 phr)	91.93 ± 0.74
NR _{SBA} (50 phr)	100.68 ± 0.91
NR _{CB} (50 phr)	61.24 ± 1.21

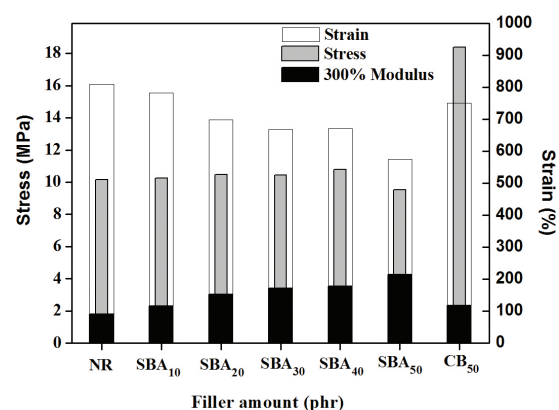


Figure 5. Values of stress versus strain in rupture point and modulus at 300% of deformation of the NR composition in function of SBA content.

Figure 4. The incorporation of SBA causes an enlargement of the DMA curves attributed to the lower mobility of the chain segments from the elastomer owing interaction with the filler incorporated. The intensity of the $\tan \delta$ peaks decreases with increase of the filler amount added to the composite, attributed to the decrease on mobility of the polymeric chain^[26].

The T_g value is associated with the mobility of the main chain as well as the movements of small segments when exposed to periodic stress. The crosslink density

as well as physical interaction between the phases (filler-matrix) decreases the mobility of the polymeric chains, established according the results from mechanical analysis. T_g temperatures were also measured using DMA technique (Table 3). Slight differences around 3 °C were obtained when evaluated the increase of SBA amount on the composites which could be associated to the device parameters errors. However, it is notice that the T_g temperatures are different when compared results from DMA and DSC techniques, attributed to the fact that DMA use dynamic method which is more susceptible to movements from the polymeric chain.

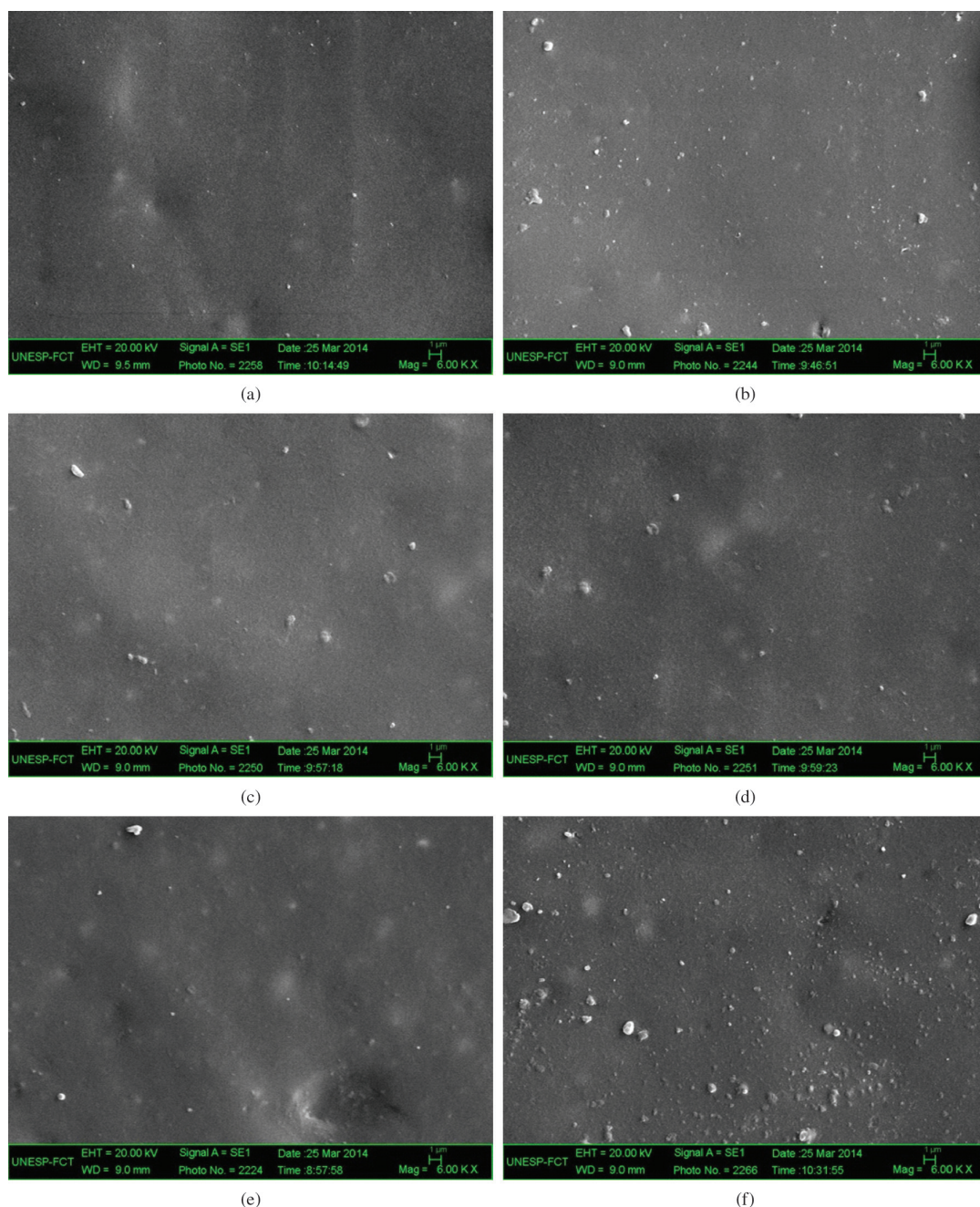


Figure 6. Scanning electronic microscope (SEM) images from (a) natural rubber and natural rubber composites with (b) 10 phr; (c) 20 phr; (d) 30 phr; (e) 40 phr; (f) 50 phr of SBA particles.

The abrasion resistance measured decreases with the SBA incorporation (Table 4). The increase on the mass loss is associated to the filler-filler interactions, generating aggregates (increases with higher compositions of the SBA particles), which origin tensions regions on the surface of the composites, decreasing the abrasion resistance. Evaluating natural rubber composites containing carbon black (commercial filler – N 330) it is notice that the

commercial filler almost unaffected the abrasion resistance. The parameters to fabrication of artifact implemented on abrasives surfaces, e.g. shoes sole, require abrasion resistance values less than 200.0 mg (mass loss) which qualify the composites NR/SBA as promissory raw material^[27].

The mechanical properties of the NR/SBA composites are reported in Figure 5. The tensile properties are given in

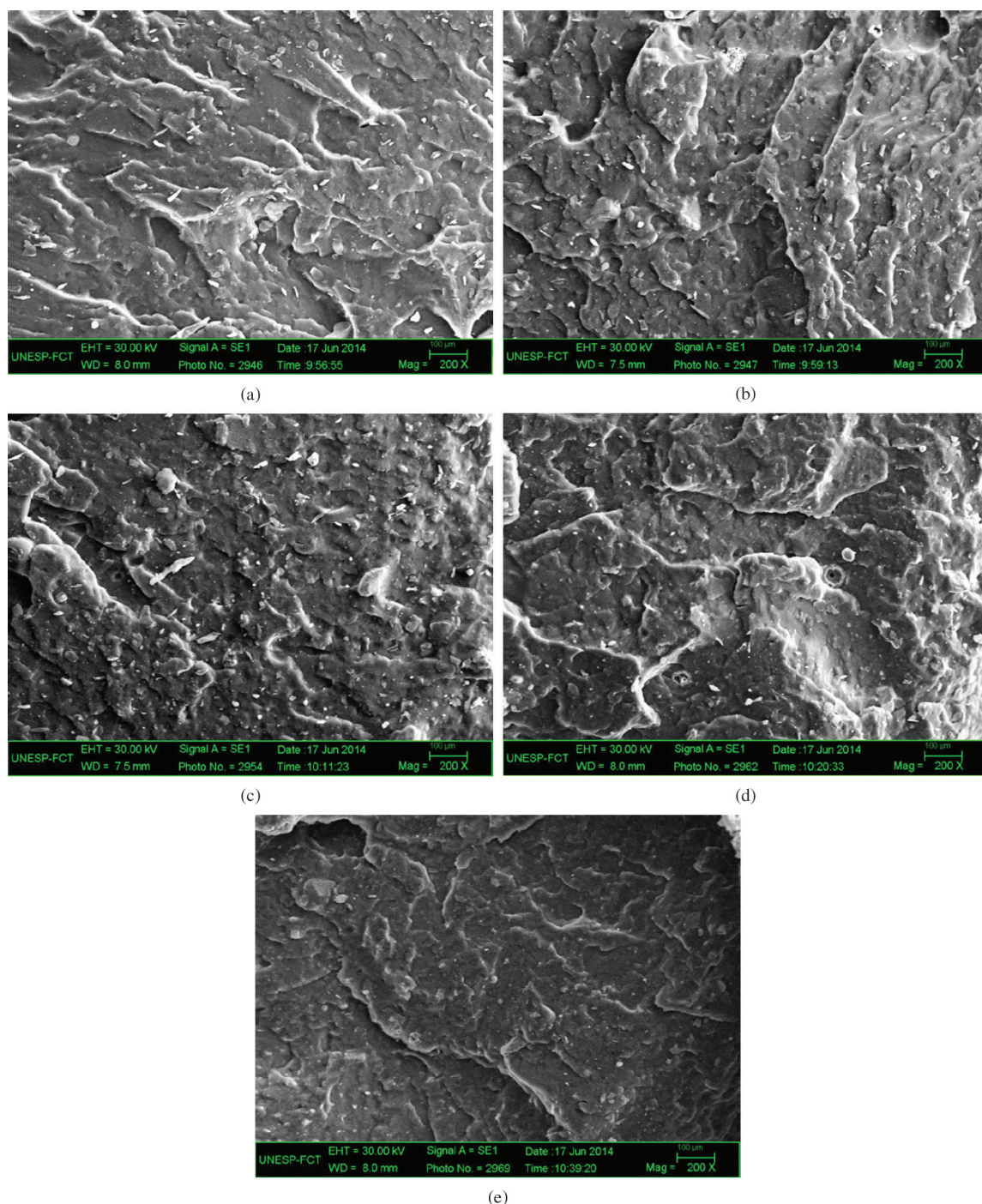


Figure 7. Scanning electronic microscope (SEM) images from cross-section of natural rubber composites with (a) 10 phr; (b) 20 phr; (c) 30 phr; (d) 40 phr; (e) 50 phr of SBA particles.

terms of 300% modulus, strength and elongation at break. For the composites investigated in this study, the amount of incorporated filler increases the modulus values as well as the strength at break for compositions until 40 phr of SBA particles attributed to the high degree of interfacial adhesion between filler-polymer. In Figure 6 the scanning electron microscope (SEM) images from the surface of the NR/SBA composites shows homogeneity, i.e. surfaces without imperfections as well as the natural rubber covering the SBA particles, demonstrating quality of particles dispersion on polymeric matrix. Nevertheless, NR/SBA (50 phr) composites evidence reached limited of SBA amount, i.e. the fillers excess promoting the migration of zinc oxide to the composites surface. Moreover, the critical concentration of the SBA particles is assured in terms of the decrease of the strength at break obtained from mechanical evaluation of the composites NR/SBA (50 phr). As mentioned before, increasing the amount of SBA particles increase the filler-filler interactions (aggregates) promoting tension as well as failures on polymeric structure, decreasing the mechanical response^[28].

The cross-section microscopy images (Figure 7) shows similar features for all NR_{SBA} composites, i.e. high level of roughness, which represent higher ductility. The morphology from cross-section is generated because of plastic deformation during the fracture process. The plastic deformation is enhanced with the incorporation of SBA particles as well observed during the mechanical tests. Cross-section images present the SBA particles well covered by natural rubber.

When comparing the SBA particles with carbon black as fillers for natural rubber it is notice higher modulus values. The stress-strain results qualify the NR/SBA composites as implemented raw material to artefacts production^[27]. In fact, the reinforcement effect of a filler, at low elongations, is slight influenced by it dispersion, explaining the stress-strain results. When considerate high strain (break point) the contribution from dispersive homogeneity of the fillers is evidentially because the rupture depends on the amount of structural failures or inhomogeneities in the natural rubber composites^[29].

Conclusion

In this study we have reported a new method of recycling and redirecting the waste (SBA) from sugarcane industries and the use of cheap filler to natural rubber. The composites were prepared without changing their chemical properties when SBA was incorporated, as shown by DSC technique and the modulus at 300% increases with the amount of SBA incorporated.

Acknowledgements

The authors acknowledge FAPESP, INEO, NanoBioMed and NanoBioNet groups, for financial support.

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Received: Sept. 09, 2013

Revised: Mar. 25, 2014

Accepted: June 09, 2014