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Novel Mineral and Organic Materials from Agro-Industrial Residues as Fillers for Natural Rubber

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Abstract Bio-based materials are being developed, increasingly, because of the need for sustainable, environmentally friendly, processes and products. We have made natural rubber composites containing low cost fillers derived from agro-industrial wastes, namely, eggshells, carbon fly ash, processing tomato peels and guayule bagasse. Composites manufactured with 35 phr (parts per hundred rubber) of carbon black (particle size 108 ± 31 nm) were used as a reference filled material. The amount of carbon black was gradually replaced by a specific waste-derived macro (<300 µm diameter) or micro (<38 µm diameter) filler. Despite differences in particle size distribution and surface chemistry, the tensile properties of micro sized tomato peels composite were similar to those of the carbon black reference composite. Composites manufactured using micro sized particles at low loadings (5 and 10 phr) of carbon fly ash and eggshells, as co-fillers with carbon black, also demonstrated comparable tensile results to those of composites manufactured solely with carbon black. Hierarchical cluster analysis partitioned the data into five groups of composites having statistically similar mechanical properties. Composites containing micro sized particles at low loadings (5 and 10 phr) were grouped in clusters 1, 2 and 5. These clusters gathered composites with the highest tensile strength and 300 % modulus. As the amount of non-carbon black filler increased above 10 phr and up to 35 phr (maximum filler loading used), the composites became weaker than the carbon black filled composites and modulus decreased.

Introduction

Natural rubber is an elastomeric material that possesses unique properties such as self-reinforcement, abrasion, tear, and impact resistance, among others [1–3]. These properties are required in enumerable applications including tires, conveyor belts, gaskets and hoses [4]. Further improvements in rubber inherent properties are obtained by the addition of reinforcing agents like carbon black and silica, neither of which is currently derived from renewable sources [3] apart from a tiny amount of carbon black. Carbon black is the oldest, most widely used and studied filler for rubber compounds [5].

There is increasing interest in developing bio-based materials in order to reduce dependency on fossil fuels, valorize agricultural and industrial residues, and generate more sustainable materials while concomitantly minimizing pollution. Nevertheless, studies on natural rubber and plastic composites in the last decade have mainly focused on cellulosic fillers [6–10] due to their renewable characteristics, degradability, abundance and diversity of sources, as well as for the high mechanical properties of these naturally structural materials [11–13]. Little evaluation has been done on other waste streams that could confer high performance characteristics to composites.

Four abundant agro-industrial residues, processing tomato peels, carbon fly ash, guayule defoliated stem

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bagasse (potentially abundant) and eggshells, were tested in this study as alternative fillers for natural rubber composites. Some waste-derived materials, such as eggshells [14], rice husks [15] and fibers from bamboo [7] and sugar cane [10] have been evaluated singly but not in direct comparison with other materials. This paper explores the diversity of mechanical properties obtained for different rubber composites as result of their different composition and loading, using the waste fillers as partial and full replacements of petroleum-derived carbon black. Tomato peels and eggshells are significant solid wastes generated from the food processing sector. In 2012, 12 million metric tons of processing tomatoes were harvested in the United States [16] generating a processing waste of 437,574 metric tons of skins, while 95.176 billion eggs were produced in the United States in 2013 [17] generating 596,754 metrics tons of shells. On the other hand, guayule bark bagasse is obtained as a by-product of latex extraction from the guayule shrub, and is not currently produced in large amounts. However, guayule is an important source of natural rubber, demand for which is increasing due to the lack of allergic responses associated with the latex, compared to the traditionally used natural rubber latex [18]. Carbon fly ash is a readily available and cheap material from power plants fueling many manufacturing processes.

The utilization of low cost materials as fillers could reduce the final cost of rubber products; however, due to the demanding conditions under which many natural rubber products are used, the properties of the composite materials must be evaluated to ensure that the composites meet or exceed performance requirements. These requirements suggest that reinforcing fillers will be required and that diluent fillers may have limited utility. Primary factors to consider when selecting reinforcing fillers are particle size, loading, structure, and surface activity [19]. These factors affect the dispersion of the filler in the rubber matrix, as well as filler–filler and polymer–filler interactions, and determine the final physical properties [5]. The aim of this study is to analyze natural rubber composite properties achieved with different polymer–filler interfaces, particle sizes and loadings of waste-derived fillers.

Experimental

Materials

Hevea natural rubber (grade SMR-20), purchased from Centrotrade (Chesapeake, VA), was used as the polymer matrix. Compounding chemicals, namely, zinc oxide, stearic acid, sulfur, the vulcanization accelerator butyl benzothiazole sulfonamide (TBBS), and carbon black N330 (mean particle size: 108 nm, SD 31.42 nm), were

purchased from HB chemicals (Twinsburg, OH). The waste filler raw materials were generously donated as follows: eggshells (ES) by Troyer's Home Pantry (Apple Creek, OH), carbon fly ash (CFA) by Cargill Salt (Akron, OH), processing tomato peels (TP) by Hirzel Canning Co & Farms (Toledo, OH), and guayule bagasse (GB) was generated as a co-product of latex extraction at our facility from guayule shrubs donated by PanAridus (Casa Grande, AZ).
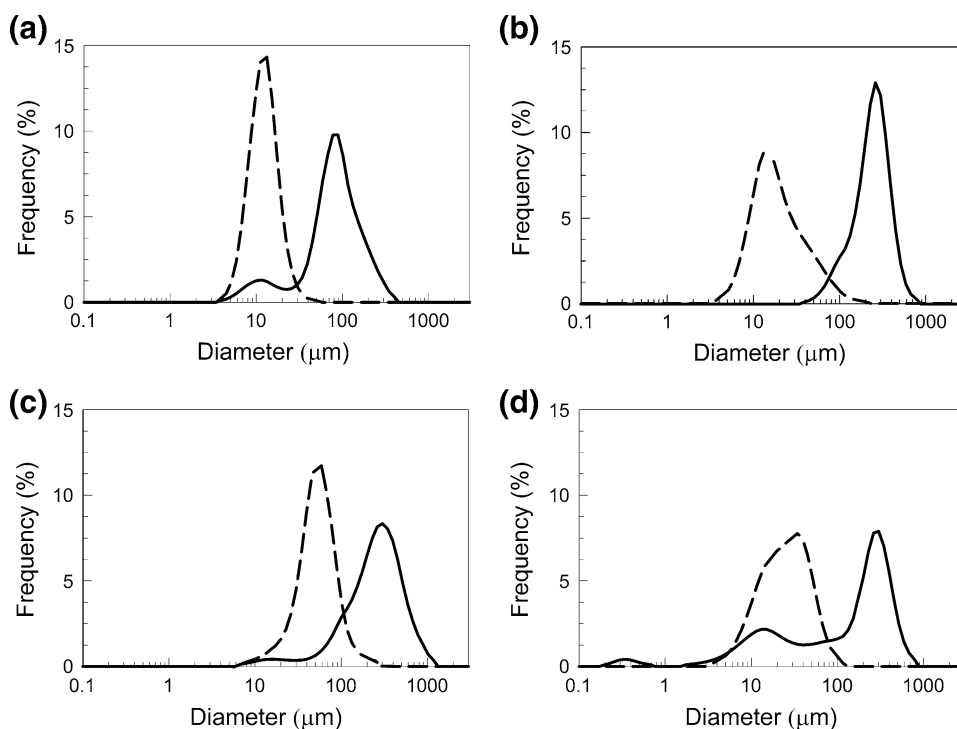
Preparation of Fillers

Raw materials were dried at 55 °C and then ground to macro (diameter (d) of 300–38 μm) and micro (d of 38–100 nm) particle sizes. The macro fillers were dry milled using a mini Wiley mill, Thomas Scientific (Swedesboro, NJ) and sieved using a sieve with a mesh size of 50 (sieve opening 300 μm), Fisher Scientific (Pittsburgh, PA). The micro fillers were wet-milled in a five liter ball mill, U.S. Stoneware (East Palestine, OH), dried, then dry-milled using a Planetary Ball Mill 100, Glen Mills (Clifton, NJ) and sieved using a mesh size 400 (sieve opening 38 μm). Particle size distributions were verified using a Particle size analyzer LA-950 V, Horiba Scientific (Irvine, CA) (Fig. 1). Filler bulk densities were determined by weighing a known volume of each filler and calculating the bulk density as mass/volume occupied (Table 1).

Composite Preparation

The effect of different types of waste-derived fillers, particle size and filler loading, were determined using a standard compound formulation initially containing 35 phr of carbon black N330 and no other filler. Carbon black was gradually replaced by each specific waste-derived filler until no carbon black remained (Table 2). Fillers and compounding ingredients were incorporated into 790 g of rubber through mastication using a Farrel BR lab mixer, Rubber City Machinery Corporation (Akron, OH). The mixer chamber was charged with rubber blocks (approximately 5 cm cubes), followed by lowering the ram to allow the rubber to knead for 40 s at 6.3 rad/s. Filler and stearic acid were then added and mixed until the mix temperature reached 82 °C. Finally, the remaining compounding ingredients were added, the rotor speed was increased to 9.4 rad/s and the batch was allowed to mix until it reached 99 °C. The ram was raised during the mixing to sweep materials deposited from orifices. The hot mix was discharged from the mixer, and then milled while still hot using a two-roll EEMCO lab mill, roll diameter 15.24 and 33.02 cm face width, Rubber City Machinery Corporation (Akron, OH). The samples were milled until a bank of rubber formed in between the rollers, and then three

Fig. 1 Macro ——— and micro
- - - - sized fillers' particle size
distribution. **a** Carbon fly ash;
macro (median 76.20 μm, mean
89.32 μm, SD 61.94 μm), micro
(median 11.25 μm, mean
12.12 μm, SD 4.93 μm),
b eggshells; macro (median
230.33 μm, mean 241.46 μm,
SD 111.01 μm), micro (median
16.07 μm, mean 23.19 μm, SD
20.79 μm), **c** guayule bagasse;
macro (median 243.10 μm,
mean 279.33 μm, SD
188.56 μm), micro (median
49.09 μm, mean 54.75 μm, SD
30.63 μm), **d** tomato peels;
macro (median 170.70 μm,
mean 179.02 μm, SD
154.91 μm), micro (median
23.08 μm, mean 26.95 μm, SD
17.00 μm)

Table 1 Filler bulk densities

Filler	Size	Density (g/cm^3)
Carbon black		0.42 ± 0.01
Carbon fly ash	Macro	0.74 ± 0.02
Carbon fly ash	Micro	0.57 ± 0.01
Guayule bagasse	Macro	0.53 ± 0.02
Guayule bagasse	Micro	0.36 ± 0.07
Eggshells	Macro	1.32 ± 0.02
Eggshells	Micro	0.79 ± 0.05
Processing tomato peels	Macro	0.69 ± 0.02
Processing tomato peels	Micro	0.60 ± 0.02

Table 2 Compounding formulations used to prepare NR composites

Material	Quantity (phr)				
Natural rubber	100				
Carbon black	35	30	25	15	0
Filler	0	5	10	20	35
Sulfur	3.5				
Zinc oxide	5				
Butyl benzothiazole sulfonamide (TBBS)	0.75				
Stearic acid	1				

24.8 cm width cuts (approximately ¾ of the distance across the rolls) were made along the face of the rubber from both the left and right sides of the mill. The rubber was cut from the mill, folded back on itself and passed through the rollers two more times. The composites were cured in an ASTM D3182 150 by 150 by 2 mm mold [20] at 160 °C and 16 tons of force, for 12 min, using a Wabash 4-post, 30 ton heated press, Rubber City Machinery Corporation (Akron, OH). After curing, the material was conditioned at room temperature for 24 h prior to assessment of tensile properties.

Materials Characterization

Composite Testing

Five dumbbell specimens of each composite were cut using ASTM Die C. Tensile properties were measured along the grain direction, according to ASTM D412 [21], using a tensiometer, Model 3366, Instron, (Norwood, MA), with a crosshead speed of 500 mm/min. The resulting properties of these composites (300 % modulus, tensile strength and elongation at break) were compared.

Fourier Transform Infrared Spectroscopy (FTIR)

The presence of functional groups on the surface of the fillers and composites was verified using a PerkinElmer Spectrum Two IR spectrometer (Waltham, MA, USA). Spectra were recorded in the range of 4000–450 cm^{-1} by accumulating 32 scans at a resolution of 2 cm^{-1}.

Table 3 Tensile properties of NR composites manufactured using micro and macro sized particles obtained from different waste derived materials

Filler type[a]	Size	Waste filler[b] (phr)	Modulus at 300 % (MPa)	SE	Modulus at 300 % means comparison[c]	Elongation at break (%)	SE	Elongation at break means comparison[c]	Tensile strength (MPa)	SE	Tensile strength means comparison[c]
Unfilled vulcanized NR		0	1.37	0.03	Q	1298	0.23	DEFGHIJ	9.96	0.28	M
Control*		0	5.83	0.09	AB	1283	0.20	DEFGHIJK	34.24	0.29	A
CFA	Macro	5	5.10	0.04	DE	853	0.55	MN	19.57	1.52	GH
CFA	Macro	10	4.73	0.04	EF	956	0.54	LMN	20.82	1.41	FGH
CFA	Macro	20	3.88	0.02	HIJ	798	0.59	N	13.60	1.44	KLM
CFA	Macro	35	2.16	0.05	OP	1442	0.22	BCDE	14.87	0.60	IJKL
CFA	Micro	5	5.65	0.06	BC	1278	0.14	EFGHIJK	28.80	0.42	BC
CFA	Micro	10	5.31	0.20	CD	1251	0.30	GHIJK	27.04	0.90	BCD
CFA	Micro	20	4.39	0.12	FG	1433	0.14	BCDEF	27.49	0.34	BCD
CFA	Micro	35	2.70	0.05	MN	1526	0.29	AB	22.09	0.53	EFG
GB	Macro	5	5.24	0.03	CD	1156	0.18	IJK	25.87	0.46	CDE
GB	Macro	10	4.53	0.04	FG	1201	0.28	HIJK	22.09	0.95	EFG
GB	Macro	20	3.61	0.07	IJ	1282	0.17	DEFGHIJK	17.95	0.42	HIJ
GB	Macro	35	2.48	0.02	MNO	1442	0.34	BCDE	13.21	0.47	LM
GB	Micro	5	4.05	0.04	GHI	1292	0.15	DEFGHIJ	27.23	0.36	BCD
GB	Micro	10	3.39	0.03	JKL	1367	0.04	BCDEFGH	24.69	0.21	DEF
GB	Micro	20	1.90	0.38	PQ	1491	0.83	AB	17.40	0.54	HIJK
GB	Micro	35	3.01	0.03	KLM	1480	0.12	BC	18.19	0.28	GHIJ
ES	Macro	5	5.10	0.08	DE	1234	0.21	GHIJK	29.63	0.32	BC
ES	Macro	10	4.48	0.17	FG	1306	0.18	CDEFGHI	26.60	0.72	BCD
ES	Macro	20	2.86	0.02	LM	1451	0.25	BCD	22.11	0.40	EFG
ES	Macro	35	1.88	0.01	P	1662	0.29	A	18.61	0.54	GHI
ES	Micro	5	5.54	0.04	BCD	1154	0.23	IJK	28.99	0.23	BC
ES	Micro	10	4.50	0.08	FG	1396	0.31	BCDEFG	30.05	0.50	B
ES	Micro	20	3.46	0.12	JK	1521	0.26	AB	28.72	1.14	BCD
ES	Micro	35	2.26	0.06	NOP	1173	0.54	KL	11.73	1.03	LM
TP	Macro	5	4.36	0.06	FGH	1265	0.34	EFGHIKJ	27.24	0.55	BCD
TP	Macro	10	2.92	0.02	LM	1265	0.25	FGHIJK	19.64	0.44	GH
TP	Macro	20	2.79	0.02	MN	1162	0.12	IJK	14.38	0.23	JKL
TP	Micro	5	5.32	0.08	BCD	1123	0.17	JKL	28.27	0.33	BCD
TP	Micro	10	6.65	0.10	A	1130	0.23	GHIJKLM	31.76	0.35	ABC

Each value is the mean of five samples

* A composite made using 35 phr of carbon black was used as the reference material

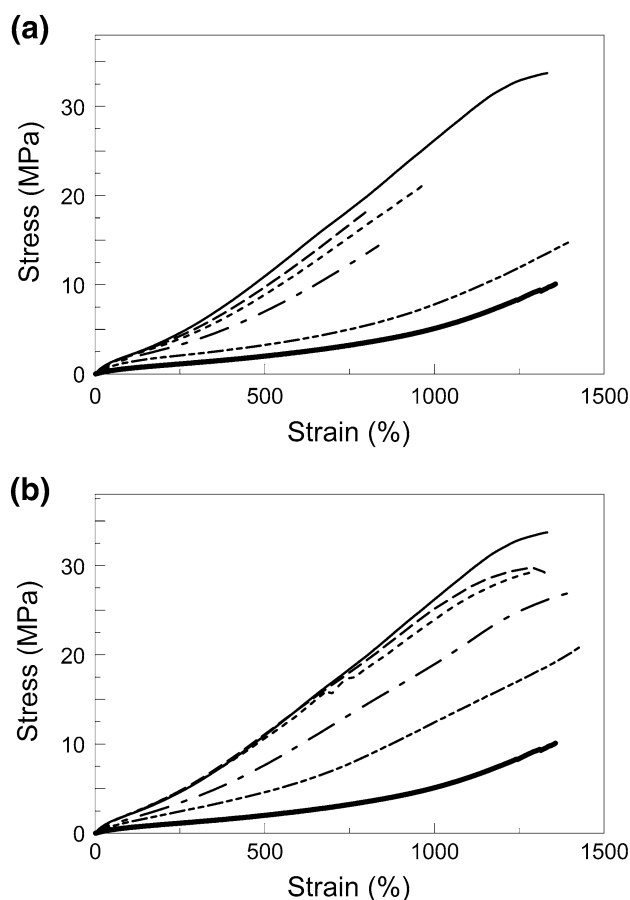[a] Filler type: carbon fly ash (CFA), guayule bagasse (GB), eggshells (ES), processing tomato peels (TP)

[b] Table reports the amount of non-carbon black filler in the sample. Total amount of filler (carbon black plus non-carbon black), in all samples was 35 phr

[c] Multiple means comparison Tukey–Kramer test, at a significance level α of 0.05. Samples that do not share a common letter are significantly different

Scanning Electron Microscopy (SEM)

A Hitachi S-3500 N scanning electron microscope (Tokyo, Japan), operated in a high vacuum, was used to investigate the morphology of the different types of materials and dispersion of the fillers within the polymer matrices. Cross sections of each composite sample at the fracture surface were cut and washed with an ethanol solution 70 %, to eliminate surface contamination. The samples were sputter-coated with a thin layer of platinum (0.2 KÅ) by an Anatech Hummer 6.2 Sputtering system prior to analysis in order to improve their conductivity, allowed to dry and imaged.

Fig. 2 Stress versus strain curves of NR composites made with different amounts of carbon fly ash, using **a** macro size particles, **b** micro size particles. Total filler loading is 35 phr. As the waste filler loading increases the carbon black filler decreases by the same amount. Waste filler loading ——— 0 phr, – – – – 5 phr, –––––– 10 phr, —·—·· 20 phr, —··—· 35 phr, ▬▬ Unfilled NR

Fig. 3 Stress versus strain curves of NR composites made with different amounts of guayule bagasse, using **a** macro size particles, **b** micro size particles. Total filler loading is 35 phr. As the waster filler loading increases the carbon black filler decreases by the same amount. As the waster filler loading increases the carbon black filler decreases by the same amount. Waste filler loading ——— 0 phr, – – – – 5 phr, –––––– 10 phr, —·—·· 20 phr, —··—· 35 phr, ▬▬ Unfilled NR

Statistical Analysis

Cluster analysis was done in order to group composites with similar mechanical properties. In this multivariate analysis, every sample was described by results obtained from the three different response properties: i.e. 300 % modulus, tensile strength and elongation at break. Euclidian distance was used to measure the similarity between the treatments. Ward's method was used as the linkage method. Multiple means comparison Tukey–Kramer test, at a significance level α of 0.05, was performed, in order to further compare the resulting groups.

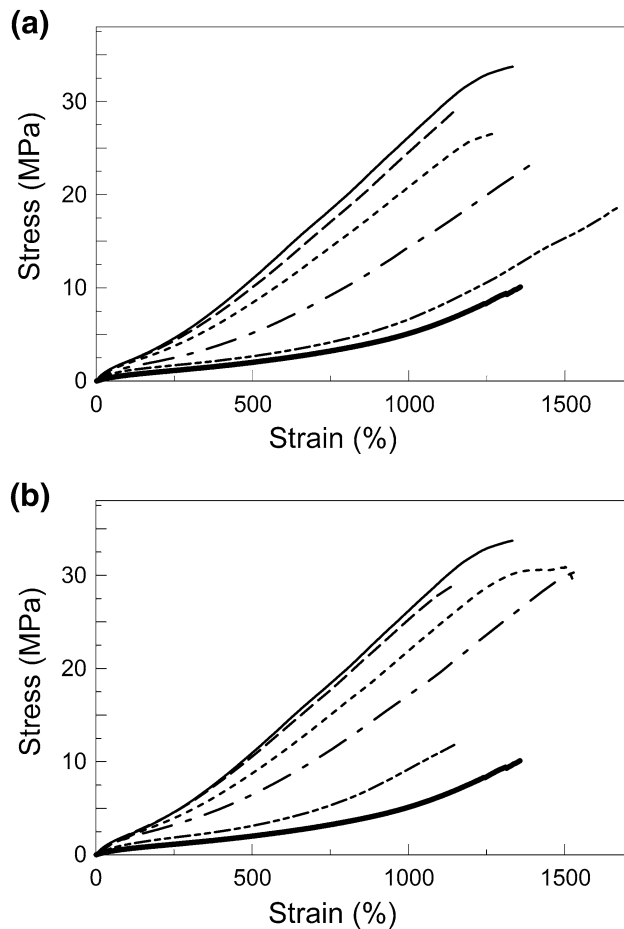## Results

Tensile Properties of Composites

Considering all three properties measured, the overall results indicate that some reinforcing effects were obtained at low loadings (5 and 10 phr) of micro sized non-black fillers, especially CFA, ES and TP. Composites manufactured by partially replacing carbon black with these materials had tensile properties comparable to those of the carbon black composites. Particularly, composites made by partially replacing carbon black with TP, were reinforced similarly to carbon black alone. This is important considering the renewable character of these materials, which carbon black lacks, and their probable lower cost.
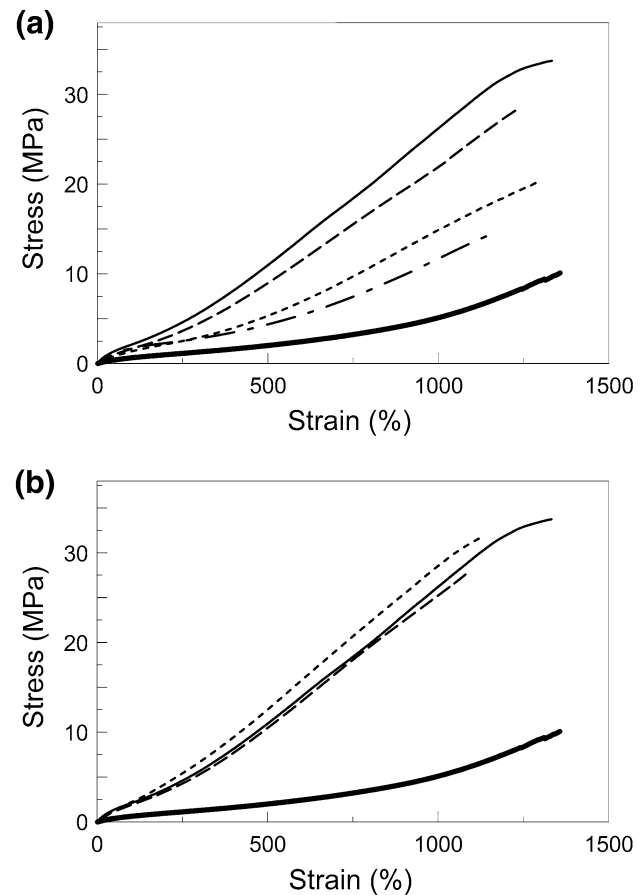
As the amount of non-carbon black fillers was increased above 10 phr, a substantial increase in elongation at break, and decrease in 300 % modulus and tensile strength of the composites was observed (Table 3). Higher values of 300 % modulus and tensile strength were achieved by composites made with micro, rather than macro, sized particles. In general, broader particle size distributions were observed for macro particles compared to micro sized

(a)

(b)

Fig. 4 Stress versus strain curves of NR composites made with different amounts of eggshells, using **a** macro size particles, **b** micro size particles. Total filler loading is 35 phr. As the waster filler loading increases the carbon black filler decreases by the same amount. Waste filler loading ——— 0 phr, – – – – 5 phr, ------· 10 phr, —·—·· 20 phr, —··—· 35 phr, ▬▬▬ Unfilled NR

(a)

(b)

Fig. 5 Stress versus strain curves of NR composites made with different amounts of processing tomato peels, using **a** macro size particles, **b** micro size particles. Total filler loading is 35 phr. As the waster filler loading increases the carbon black filler decreases by the same amount. Waste filler loading ——— 0 phr, – – – – 5 phr, ------· 10 phr, —·—·· 20 phr, —··—· 35 phr, ▬▬▬ Unfilled NR

particles (Fig. 1). Extreme particle size values under the left side of the curve of macro size distributions were considered for the analysis of the result; however, these small portions of material do not seem to drastically affect the overall resulting properties.

Composites manufactured with low loading (5 phr) of CFA, ES and TP, with 30 phr carbon black, had very similar values of 300 % modulus to those of composites made with carbon black alone, for both macro and micro sized particles. Furthermore, 300 % modulus of composites containing 5 phr micro sized CFA, ES and TP, as well as the 10 phr micro sized TP composite, were not significantly different from the mean 300 % modulus of the carbon black reference composite. Similarly, the composites with the highest tensile results were those containing 10 phr of micro sized TP and ES, and 5 phr of macro sized ES, with tensile strengths of 31.76, 30.05 and 29.63 MPa,
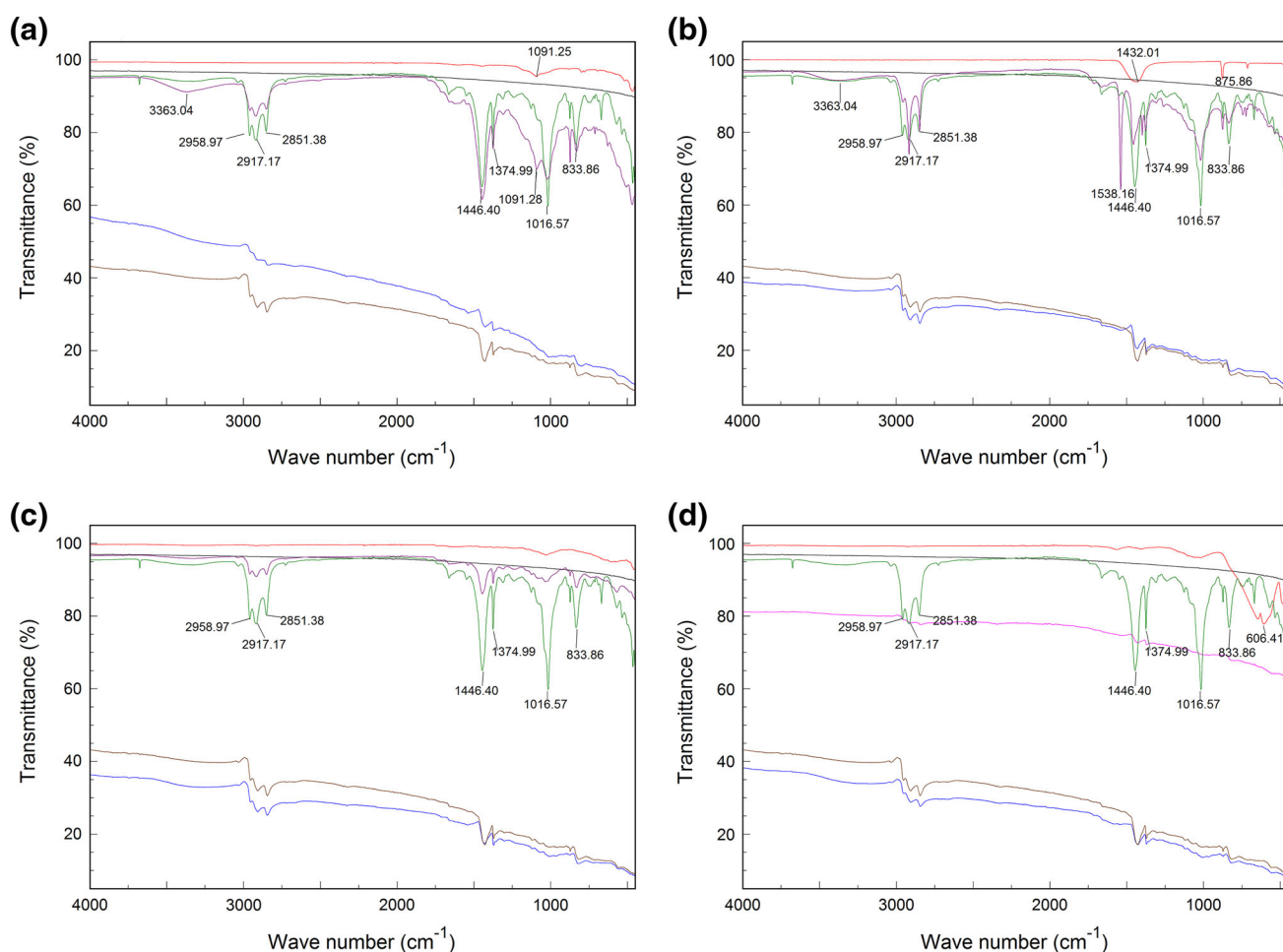
respectively. The mean tensile values of 10 phr of micro sized TP and ES, and 5 phr of macro sized ES were not significantly different from each other, but only 10 phr of micro sized TP was not significantly different from carbon black alone 34.24 MPa (Table 3).

As seen from the stress versus strain curves (Figs. 2, 3, 4, 5), for composites made with macro particle size (plot a) and micro particle size (plot b), as the amount of non-carbon black filler was increased, the composites behaved more like an unfilled vulcanized rubber, represented by the thick solid line (Figs. 2, 3, 4, 5). Typical strain-induced crystallization also was observed in composites containing only non-carbon black fillers at elongation greater that 700 %.

The high stiffness of composites containing high loadings (20 and 35 phr) of micro sized TP and 35 phr of macro sized TP impeded the processing of the material, compromised its integrity, and data are not shown for these unsuccessful samples.

(a)

(b)

(c)

(d)

Fig. 6 FTIR spectra of fillers (*red*), carbon black (*black*), unfilled rubber (*green*), 35 phr carbon black composite (*brown*), 5 phr non-black composites (*blue*) and 35 phr non-black composites (*purple*).

a carbon fly ash, **b** eggshell, **c** guayule bagasse, **d** processing tomato peels (Color figure online)

FTIR Spectral Analysis

Most of the functional groups found in the rubber composites were the same as those found in unfilled vulcanized rubber, represented by the green line (Fig. 6). Variations in the spectra are due to changes in the concentration of the functional groups in the composites, due to the addition of fillers. A broad peak around 3390–3100 cm^{-1}, possibly due to the O–H bond from stearic acid, was observed in the rubber compounds [22]. Absorption bands characteristic of natural rubber were observed around 2960–2800 cm^{-1} due to the stretching frequency of methyl and methylene [23, 24]. Bending vibrations of methylene and methyl bonds are represented by peaks at 1446 and 1370 cm^{-1} [24, 25]. In addition, peaks at 1016 and 833 cm^{-1} may be due to C–C stretching and to isoprene double bond bending, respectively [26–28]. On the other hand, a peak at 1091 cm^{-1}, only present in CFA and CFA composites, is due to Si–O
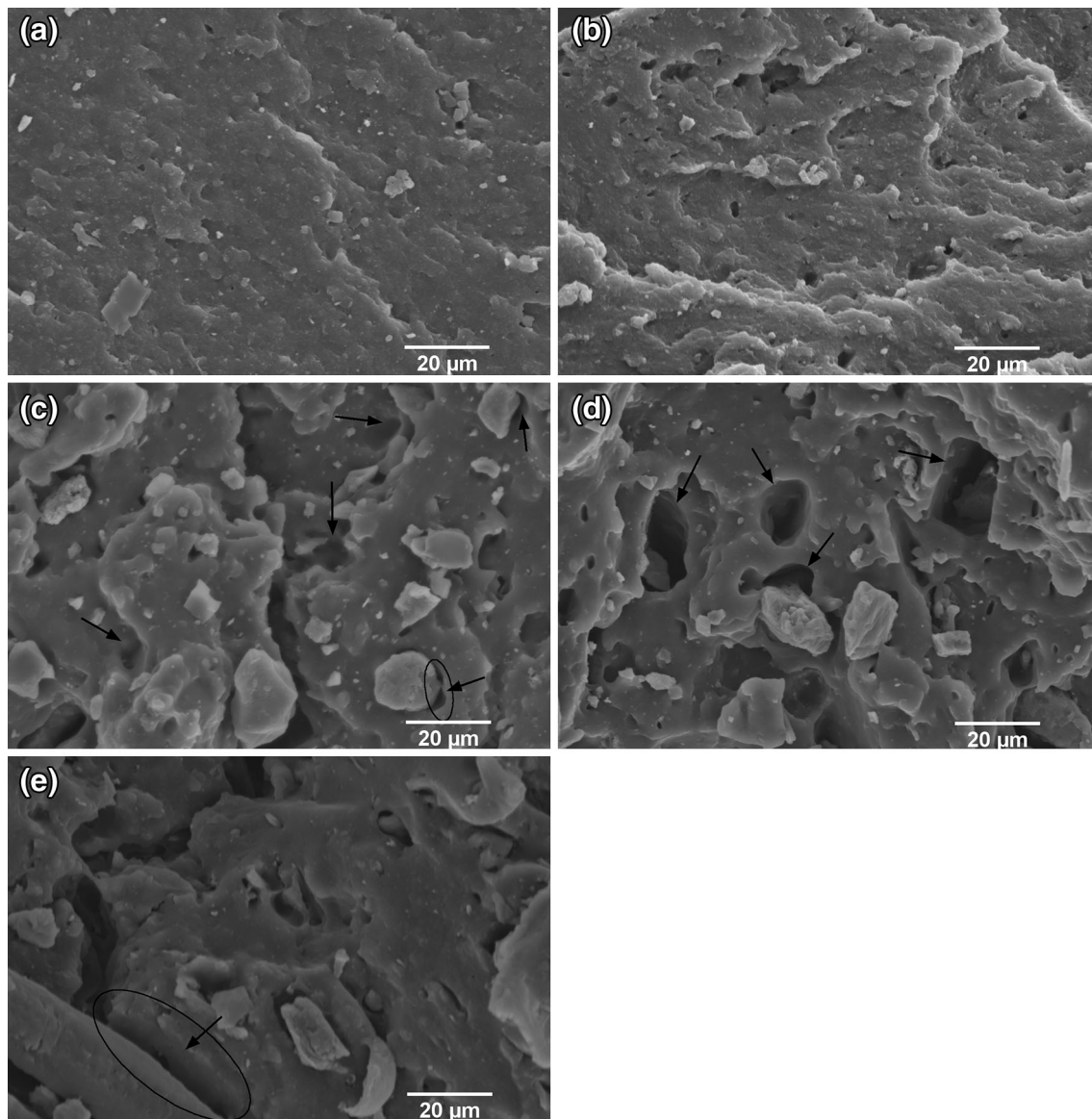
vibration [29], while peaks at 1432 and 875.86 cm^{-1} present in ES are due to asymmetric stretching and bending of CO_3 from calcium carbonate [14, 30]. Finally, the broad band at 606 cm^{-1} observed in TP may be due to wagging of NH_2 found in amides [31].

Analysis of Composite Morphology

Differences in interfacial interactions between natural rubber and the various types of filler were reflected in the composite morphology (Fig. 7). Carbon black composites (Fig. 7a) had a uniform surface, and neither agglomerations of the filler, nor gaps within the polymer matrix were observed. The micro sized TP composite (Fig. 7b) had a uniform surface similar to carbon black alone, indicating similarities between carbon black and TP composite morphology, that further explains the resultant mechanical properties.

In contrast, the presence of several gaps within the composites made with the other fillers, and smooth surfaces

Fig. 7 SEM micrograph of NR composites with **a** carbon black, **b** processing tomato peels, micro, 10 phr, **c** carbon fly ash, micro, 20 phr, **d** eggshells, micro 20 phr, **e** guayule bagasse, micro, 20 phr

around the fillers indicates poor interfacial adhesion of the polymer with the other fillers (Fig. 7c–e).
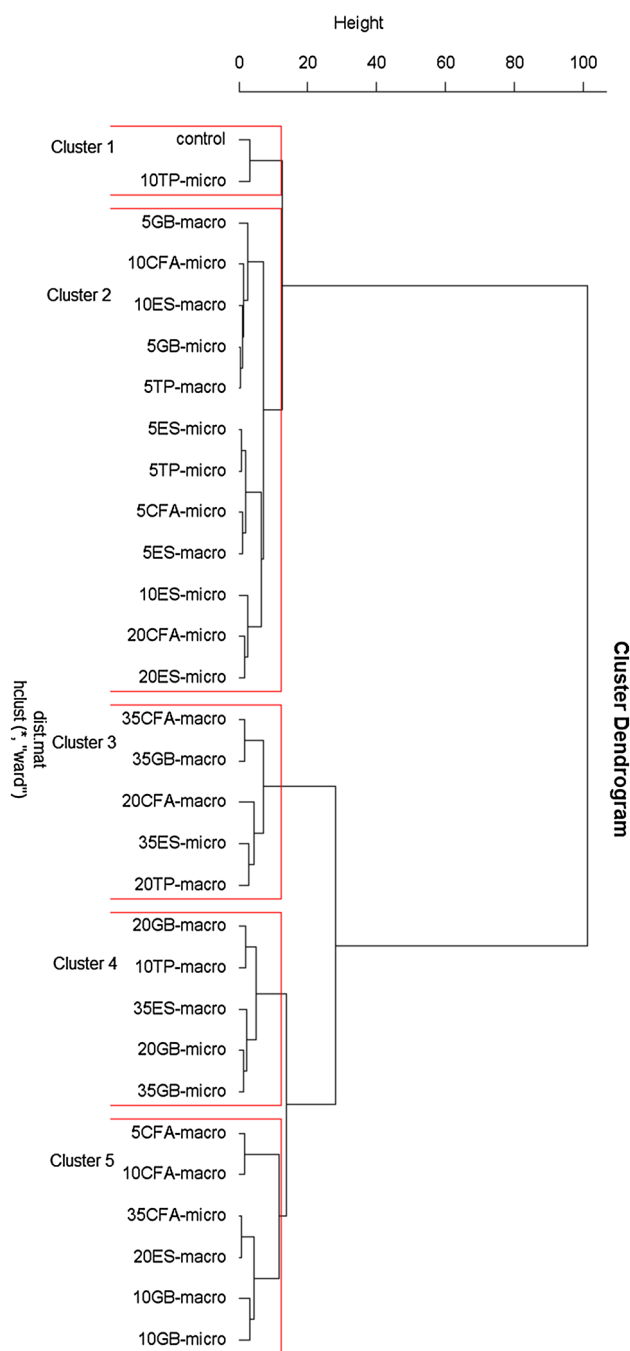
Statistical Analysis

Five homogeneous groups with common characteristics were obtained by dividing the dendrogram obtained from cluster analysis at a distance level of 12 (Fig. 8). Cluster 1 includes composites made with carbon black and 10 phr micro sized TP. Samples in this cluster possessed the highest tensile strength and 300 % modulus and middle values of elongation at break. Cluster 2 groups the largest number of samples. Nearly 70 % of the samples in this cluster contained micro sized particles at low loadings (5 and 10 phr). These samples

had high tensile strength and 300 % modulus (not as high as cluster 1) and middle to high values of elongation at break. Based on the mechanical properties, this cluster is more similar to cluster 1 than to the other clusters. Multiple mean comparisons performed for the response variable tensile strength indicated that there is not a significant difference between the mean tensile strength of composites in cluster 1. The analysis also showed no significant difference between the mean tensile strength of composites containing 10 phr of micro sized TP and composites in cluster 2. However, there is a significant difference between the mean tensile strength of composites made with carbon black and composites in cluster 2.

Cluster 3 groups composites manufactured using macro sized particles at high loadings (20 and 35 phr). The

Fig. 8 Dendrogram obtained by hierarchical clustering analysis of 30 composite formulations
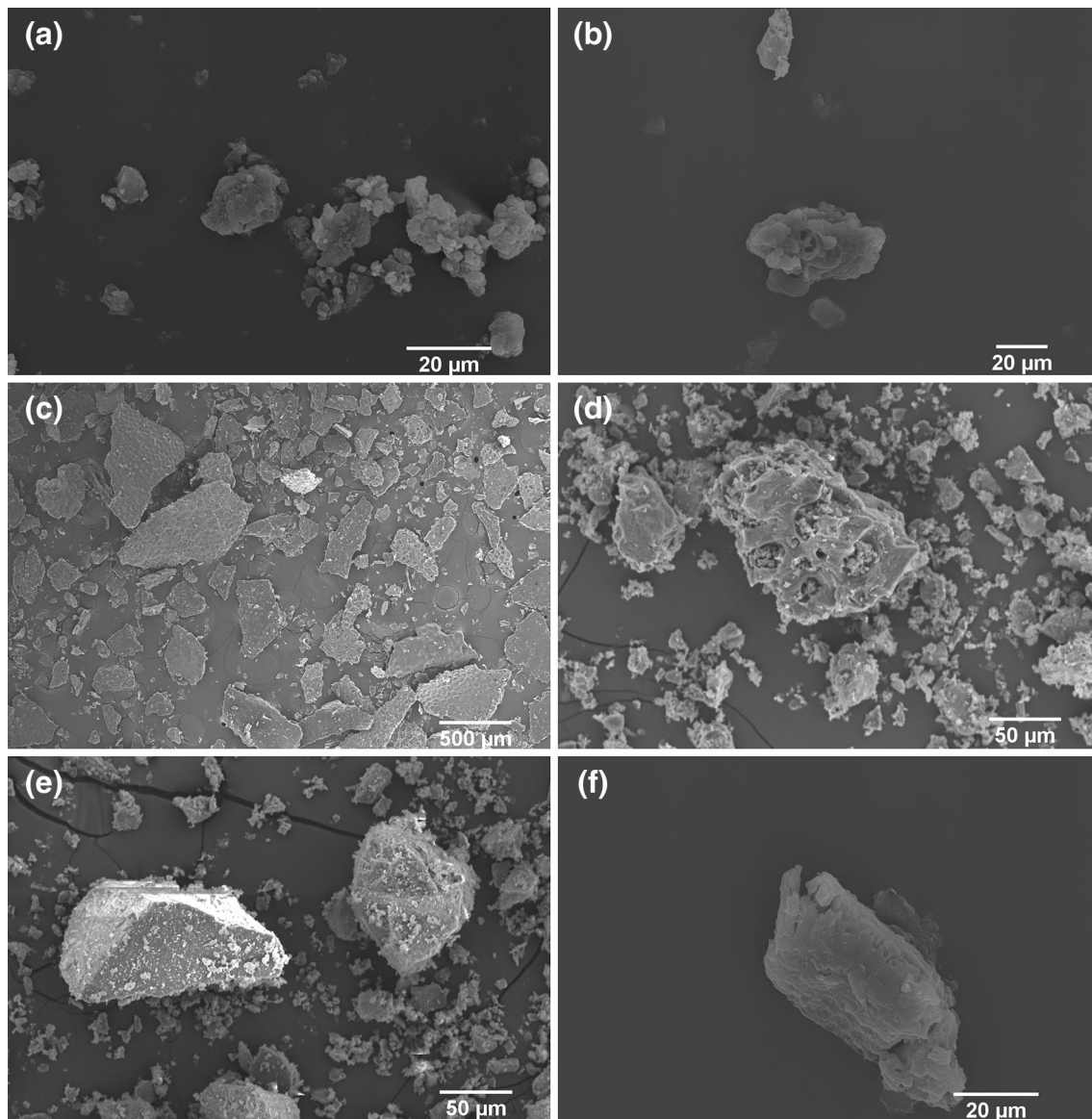
Although the different fillers were scattered among the different clusters, 75 % of composites made with the two mineral fillers (ES and CFA), were grouped in cluster 2, and 5. The clustering of the organic materials was mostly influenced by filler loading; composites containing loadings of 5 and 10 phr were grouped in cluster 2 and 5, while composites containing 20 and 35 phr were placed in clusters 3 and 4.

Discussion

Composites made by partially replacing carbon black with TP were reinforced similarly to carbon black alone, possibly due to similarities in particle structure. At a micro scale, TP particles are in the form of agglomerates of small granules (Fig. 9a), similar to carbon black structure (Fig. 9b). This particle structure is unique to these two fillers among the fillers used in this study (Fig. 9), and contributes to the reinforcing of the materials due to a combination of small particle size along with a high degree of irregularity that determines the restriction of the chain motion under the applied strain. This behavior is not observed in macro sized TP particles because at this larger scale the material presents a laminar shape (Fig. 9c) and possesses less surface area.

The structure of the mineral fillers used also influenced their reinforcing effect. ES and CFA particles possess a high surface area due to roughness and porosity of the materials (Fig. 9d, e). ES porosity is the consequence of naturally occurring gas exchange pores [14]. The porosity promotes a wetting effect that provides better interfacial adhesion between the polymer and the filler. The presence of a new peak in at 1538 cm^{-1} in the spectra of ES composites (Fig. 6b) indicates that calcium stearate has been formed by chemical adsorption of stearic acid onto the ES calcium carbonate [32]. Surface modification of calcium carbonate with stearic acid improves the hydrophobicity of the filler [33, 34], making it more compatible with the rubber. This change in the surface chemistry of the filler leads to better polymer–filler interaction and contributes to the observed reinforcing effect of ES [35].

In contrast, naturally occurring resins in GB [36] had an impact on the final mechanical properties of GB composites. These resins potentially add a plasticizing effect, which would increase the ductility of the material. Discrepancies in particle size distribution within a particle size range also may have contributed to the observed results. Micro sized GB had the highest proportion of larger particles, while micro sized TP, ES and CFA contained smaller particles. Bigger particles have less surface area per unit weight than smaller particles: this decreases the reinforcing effect and also generates flaws within the composite material.

samples had the lowest tensile strength, relatively low modulus, and middle to high values of elongation at break. Cluster 4 and 5 gather composites that showed middle values of tensile strength, middle to low values of 300 % modulus and middle to high values of elongation at break. Approximately 64 % of the composites in these groups were made using 10 and 20 phr of macro sized particles.

Fig. 9 SEM micrograph of filler particles. **a** Micro sized processing tomato peels, **b** carbon black, **c** macro sized processing tomato peels, **d** carbon fly ash, **e** eggshells, **f** guayule bagasse

It is also important to highlight the different volume fractions of fillers contained in the composites based on their bulk density. Micro sized GB possesses the lowest bulk density among the fillers used (Table 1) and, therefore, substantially larger volumes of material were needed for the preparation of the composites of similar weight loadings. This implies more filler particles are enclosed within the same volume of polymer in lower density fillers compared to the higher density fillers. Filler volumes above an optimum value promote more contact between the filler particles, which favors filler–filler interaction rather than polymer–filler interaction. This condition may lead to agglomeration of the filler and also contribute to the poor reinforcing properties observed in the results.

The lower tensile strength and 300 % modulus values achieved at high loadings (20 and 35 phr) of waste-derived fillers (Table 3) indicate a lower reinforcing effect of the non-carbon black fillers at high loadings compared to carbon black. At low filler loading the reinforcing effect of carbon black predominates in the control of the properties over the other filler, but at high loadings the reinforcing effect depends only on the non-black filler. The lower reinforcement of most of the non-black fillers is probably caused by the larger particle size compared to carbon black (lower surface area), but also may be associated with differences in surface chemistry. Besides having the smallest particles (108 nm), hence more surface area, carbon black possesses a relative non-polar surface [19], which is more

compatible with natural rubber than the more polar fillers like the cellulose in GB.

Homogeneity observed in the fracture surface of carbon black composites (Fig. 7a) is the result of good polymer–polymer filler interaction which, for carbon back, is mainly physical in nature (van der Waals forces) [5]. These weak interfacial forces allow carbon black to behave as an additional crosslinker in the natural rubber network [2] by restricting chain mobility and generating stronger and harder materials. Under strain, these adhesion forces can break and relocate allowing the material to maintain flexibility while also exhibiting resistance to deformation [19]. Given the differences in surface chemistry and particle size between the fillers studied and carbon black, this behavior is not completely matched.

The weaker polymer–filler interactions existing between some non-carbon black fillers and natural rubber is also reflected in the increased elongation at break of composites containing high loadings of the waste derived fillers. The decrease in the carbon black portion allowed more chain mobility and so a more stretchable material is obtained. Moreover, stress versus strain curves of composites containing high loadings of non-carbon black filler resemble the behavior of unfilled vulcanized rubber (Figs. 2, 3, 4, 5). In an unfilled vulcanized rubber sample, when a uniform increase in strain is applied, polymer chains are able to rearrange, and so only slight increases in stress are observed.

The partial replacement of carbon black, a nano filler, with micro sized fillers, which can be cheaply made from low cost waste materials, without loss of mechanical properties, suggests that significant cost savings may be possible by using such fillers. Nanofillers are much more difficult to manufacture at large scale than micro-fillers. It is particularly interesting that 10 phr micro-TP with 25 phr of nano-carbon black performed as well as the nano-carbon black alone.

Most of the composites manufactured from waste-derived materials in this study meet the standard physical properties required for their application in a variety of rubber products. Potential applications for the composites include rubber gaskets for general applications; tread components in P225/60R16 radial standard reference tires and insulating material, namely insulating line hose, covers, sleeves and gloves. Even if the smallest particle sizes in these fillers contribute to a disproportionate reinforcing effect on the properties, these fillers could potentially be used to manufacture rubber products with a low carbon footprint and more sustainable than conventional carbon black-filled products.

Conclusion

Agro-industrial residues are abundant solid wastes with heterogeneous composition. These characteristics make them promising fillers for the generation of natural rubber composites with reinforcing characteristics comparable to those of carbon black. Moreover, the renewable character of agro-industrial residues could improve the sustainability of natural rubber products while adding value to these waste materials. The results open the possibility of utilizing renewable waste-derived materials to reduce the amount of non-renewable carbon black in natural rubber composites. A variety of material final properties can be tailored by modifying filler characteristics, namely type, blend, particles size and loading according to the specific requirements of each end product.

References

1. Steinbüchel A (2003) Curr Opin Microbiol 6:261
2. Chenal JM, Gauthier C, Chazeau L, Guy L, Bomal Y (2007) Polymer 48:6893
3. Visakh PM, Thomas S, Oksman K, Mathew AP (2012) Compos Part A Appl Sci 43:735
4. Rodgers B, Waddell W (2013) In: Mark JE, Erman B, Roland M (eds) The science and technology of rubber. Academic Press, London, pp 417–471
5. Fröhlich J, Niedermeier W, Luginsland HD (2005) Compos Part A Appl Sci 36:449
6. Andrio A, Compañ V, Reis-Nunes RC, López ML, Riande E (2000) J Membr Sci 178:65
7. Ismail H, Edyham MR, Wirjosentono B (2002) Polym Test 21:139
8. Jacob M, Thomas S, Varughese KT (2004) Compos Sci Technol 64:955
9. Bai W, Li K (2009) Compos Part A Appl Sci 40:1597
10. Bras J, Hassan ML, Bruzesse C, Hassan EA, El-Wakil NA, Dufresne A (2010) Ind Crop Prod 32:627
11. Bendahou A, Kaddami H, Dufresne A (2010) Eur Polym J 46:609
12. Pasquini D, de Morais Teixeira E, da Silva Curvelo AA, Belgacem MN, Dufresne A (2010) Ind Crop Prod 32:486
13. Majeed K, Jawaid M, Hassan A, AbuBakar A, Abdul Khalil HPS, Salema AA, Inuwa I (2013) Mater Des 46:391
14. Intharapat P, Kongnoo A, Kateungngan K (2013) J Polym Environ 21:245
15. Ishak ZAM, Bakar AA (1995) Eur Polym J 31:259
16. Thornsbury S, Farah Wells H, Bond J (2013) Vegetable and pulses yearbook data. A report for the economic research service, USDA
17. United States Department of Agriculture, Chickens and Eggs 2013 Summary (National Agricultural Statistics Service 2014)
18. Hamilton RG, Cornish K (2010) Ind Crop Prod 31:197
19. Byers JT (2001) In: Baranwal KC, Stephens HL (eds) Basic elastomer technology. American Chemical society, Rubber division, OH, pp 82–111
20. ASTM Standard D3182-15 (2015) Standard practice for rubber—materials, equipment, and procedures for mixing standard compounds and preparing standard vulcanized sheets. ASTM International, West Conshohocken, PA. doi:10.1520/D3182-15

21. ASTM Standard D412-06a (2013) Standard test methods for vulcanized rubber and thermoplastic elastomers—tension. ASTM International, West Conshohocken, PA. doi:10.1520/D0412-06AR13

22. Pal K, Rajasekar R, Kang DJ, Zhang ZX, Pal SK, Das CK, Kim JK (2010) Mater Design 31:1156

23. Pal K, Pal SK, Das CK, Kim JK (2012) Mater Des 35:863

24. Afiq MM, Azura AR (2013) Int Biodeterior Biodegr 85:139

25. Xu T, Jia Z, Luo Y, Jia D, Peng Z (2015) Appl Surf Sci 328:306

26. Ali AMM, Subban RHY, Bahron H, Winie T, Latif F, Yahya MZA (2008) Ionics 14:491

27. Riyajan SA, Sasithornsonti Y, Phinyocheep P (2012) Carbohyd Polym 89:251

28. Fernandez-Berridi MJ, Gonzalez N, Mugica A, Bernicot C (2006) Thermochim Acta 444:65

29. Sae-Oui P, Rakdee C, Thanmathorn P (2002) J Appl Polym Sci 83:2485

30. Engin B, Demirtas H, Eken M (2006) Radiat Phys Chem 75:268

31. Sumayya A, Panicker CY, Varghese HT, Harikumar B (2008) Rasayan J Chem 1:548

32. Gönen M, Öztürk S, Balköse D, Okur S, Ülkü S (2010) Ind Eng Chem Res 49:1732

33. Mihajlović S, Sekulić Ž, Daković A, Vućinić D, Jovanović V, Stojanović J (2009) Ceram-Silikaty 53:268

34. Mihajlović SR, Vućinić DR, Sekulić ŽT, Milićević SZ, Kolonja BM (2013) Powder Technol 245:208

35. Khan I, Bhat AH (2014) In: Thomas S, Maria HJ, Joy JP, Chan CH, Pothen LA (eds) Natural rubber materials, composites and nanocomposites. The Royal Society of Chemistry, London, pp 467–487

36. Nakayama FS (2005) Ind Crop Prod 22:3