

Natural rubber/leather waste composite foam: A new eco-friendly material and recycling approach

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ABSTRACT: This article describes a new approach of recycling the leather waste (shavings) using it as filler in natural rubber foams composites. The foams were prepared using different amounts of leather waste (0–60 parts per hundred of rubber) and submitted to morphological (SEM microscopy) and mechanical analyses (cyclic stress–strain compression). The increase of leather shavings on the composite causes an increase of viscosity in the mixture, which reflects in the foaming process. This results in smaller and fairly uniform cells. Furthermore, expanded rubber has the biggest cell size, with more than 70% of cell with 1000 μm , while the composite with the higher concentration of leather has around 80% of total number of cells with 100–400 μm . The mechanical parameters were found to depend on the leather dust concentration. Moreover, the stiffness rises with the increase of leather shavings; consequently, the compression force for expanded rubber was 0.126 MPa as well as the composite with higher concentration of leather was 7.55 MPa. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41636.

KEYWORDS: composites; elastomers; foams; recycling; rubber

Received 18 March 2014; accepted 12 October 2014

DOI: 10.1002/app.41636

INTRODUCTION

Leather is a natural polymer made of collagen fibers crosslinked in a three dimensional structure. The most useful tanning process in the world is chrome-tanned, using complex salts of trivalent chromium which improves physical and chemical properties of leather.¹

The chrome-tanned process generates huge quantities of solid waste and about 600,000 tons of chromium tanned wastes are produced annually worldwide. The leather waste contains trivalent chromium that, under a series of conditions, oxidize to another form—hexavalent chromium which has been classified as carcinogen and consequently can cause serious health risks when in contact with human organism.^{2,3}

The main issues about waste generation are the volume used by the residue in landfills and the inadequate disposal, which lead to the contamination of the environment by the slow leaching of trivalent chrome. Furthermore, the cost of these deposits reaches up to US\$ 5.00/m³, increasing the manufacturing cost.⁴ One alternative is recycling through reuse, or recovery of residues, or their constituents,⁵ searching for solutions that meet the perspective of both business and environmental ambitions.

For instance, production of polymeric composites is of growing interest and an important strategy is to recycle waste materials. The rubber has emerged as a distinct template providing the improvement of performance durability and life cycle of products toward the use of waste as fillers. At present, composites implementing waste compounds as bio-filler from cassava pulp,⁶ rice husk,⁷ Pistachio shell,⁸ and solid olive waste⁹ have already been proposed.

Along with the growing use of composites materials as recycling approaches, researchers are drawing their attention toward the use of foams because of their advantages as light weight used as meat trays,¹⁰ impact damping,¹¹ thermal and acoustic insulation.^{12,13}

Some of the challenges facing the incorporation of fillers in the composition of foams are that fillers can change the viscosity of the reagents implemented as well as the kinetic parameters (temperature, concentration of reactants, contact surface) and intrinsic conditions to the foaming reaction. Therefore, physical properties (hardness, abrasion and compression resistance, tensile strength) as well as cellular structure and the density of the foam can be influenced.¹⁴

The structural response of polymer foams strongly depends on the foam density and cell microstructure such as cell size, shape,

Table I. Characterization of the Residue of Leather Waste for pH, Moisture, Ash, and Total Kjeldahl Nitrogen (TKN) by the Semi-Microkjedahl Methods According to NBR 1334

Parameter	Measure
pH	4.2
Moisture	12.2%
Ash ^a	8.03%
TKN ^{a,b}	11.8%
Chrome	3.68

^aMoisture—free basis.^bAsh—free basis.

type (open or closed) etc., as well as solid polymer properties.¹⁵ Therefore, it is not possible to obtain materials with high permeability and strength. These two factors are inversely proportional to each other. Permeability usually increases by increasing porosity, regardless of the mechanical strength.¹⁶ It must be emphasized that the final properties of this class of materials is dependent on the processing method and the consequent microstructure.^{16,17}

Moreover, leather waste has been cleverly reused to prepare composite materials. Przepiórkowska *et al.*¹⁸ developed a technique to obtain the collagen from a solid waste generated in the leather industry to effectively remove a liquid waste (tannin) from chromium-tannin wastewater using it as filler into butadiene–acrylonitrile rubber (NBR) which reaches the ideal level at only 5 parts by wt. In another work, Chronska and Przepiórkowska¹⁹ studied the effects of a mixture of chrome shavings and buffing dust on the properties of nitrile rubbers. It was examined and showed the maximum level of incorporation at 30 phr and tensile at rupture around 6.5 MPa. Ferreira *et al.*²⁰ showed the high difficulty to produce natural rubber/leather waste composites due to the weak interaction filler/polymer as well as the decrease of mechanical properties caused by fibers agglomeration. Thus, the authors used silica to decrease the effect on mechanical properties from leather incorporation, obtaining 20 phr of leather waste as maximum of residue amount which is possible to incorporate on composites without considerable loss of mechanical properties. El Sabbagh and Mohamed³ reported the increase of these properties by the enhancement of crosslink density to form homogeneous composite foaming. However, the value of tensile strength or rupture strain decreased with further loading of leather particles, which obtained a maximum tensile strength around 5 MPa. The elongation at break also decreased to half (500%) of the original size, when a maximum of 10 phr leather amount (8.23% wt) was incorporated.

Here, we report the use of leather waste, as filler in natural rubber (NR/LW) with blowing agents to produce foam. For this purpose, it was performed a comparative study about the effect of incorporating leather shavings in different quantities (20–60 phr) on the mechanic behavior by compression–decompression cycles and stress–strain tests. Morphological analyses using scanning electron microscopy (SEM) was also carried out. The NR/LW foam proposed in this work became an important alterna-

tive material for current use of expanded rubber, e.g. lining, internal insulation, sole, etc. in order to attend environmental issues related to the recycling of leather waste incorporated in the composites.

EXPERIMENTAL

Materials

Natural rubber was purchased from Industria e Comércio de Borracha e Artefatos LTda in Polini, SP (Brasil). The blowing reagent, toluenosulfohidrazina (TSH), with decomposable temperature of 105–110°C and blowing gas 115 cm³/g were produced by Chemicon S/A Indústrias Químicas; leather waste was obtained from a commercial tannery Vitapelli, located in Presidente Prudente, SP (Brasil), calcium carbonate, sulfur (S), zinc oxide (ZnO), and stearic acid (SA) were all of analytical grade and purchased from Vetec Química Fina, Ltda industry. The accelerator dibenzothiazyl disulfide (MBTS) and tetra methyl thiuram disulfide (TMTD) were of analytical grade quality, purchased from Chemicon S/A Indústrias Químicas.

Leather Waste Characterization

The leather waste was analyzed to obtain information about pH, moisture, ash, total kjeldahl nitrogen (TKN), and chromium content. Moisture was determined by heating the sample at 110°C for 12 h. Ash in dried products was determined by heating the sample at 600°C for 4 h. TKN was determined by the semi-microkjedahl methods according to NBR 13347.²¹ Chromium was determined using AAS 6 *Varia (model)* atomic absorption spectrophotometer. The results are given in Table I.

Cure Characteristic

Cure characteristic was evaluated using a Teametro ODR model from TEAM Industry, with an oscillating disk of 1° according to ASTM 2084 at a temperature of 125°C for 10 min. The obtained rheometric curve was used to calculate τ_{90} that is the optimal vulcanization time (min) (Table II). The values of t_{90} increased in proportion to the amount of leather incorporated in the composites, attributed to the acid characteristic of the waste that inhibits the action of accelerators. Similarly, the addition of leather waste increased crosslinking bonds, which were observed regarding the maximum torque amplified. Variation on minimum torque is related to the influence of leather waste in the viscosity of the composites.

Foam Composite Preparation

The leather fibers were shredded to diameters of 16 mm using a mill with rotating knives and a 30 mesh sliver from MARCONI

Table II. Rheometric Characterization, Obtained Using a Teametro ODR Model with an Oscillating Disk of 1° According to ASTM 2084 at 125°C for 10 min for Expanded Rubber and for Composites with 20, 40, and 60 phr of Leather Waste at 398 K (125°C)

Composites	M_H (dNm)	M_L (dNm)	ΔM (dNm)	t_{90} (min)
NR	19.1	1.7	17.4	6.18
NR/LW ₂₀	21.6	1.8	19.8	6.3
NR/LW ₄₀	24.4	1.9	22.5	6.43
NR/LW ₆₀	25.3	3	22.3	6.47

Table III. Formulation of Foam with Leather Waste

Ingredients (phr) ^a	Samples (phr)			
	NR	NR/LW ₂₀	NR/LW ₄₀	NR/LW ₆₀
Natural Rubber	100	100	100	100
Leather waste	0	20	40	60
Stearic Acid	2	2	2	2
Zinc oxide	4	4	4	4
MBTS ^b	1.2	1.2	1.2	1.2
TMTD ^c	0.2	0.2	0.2	0.2
Sulphur	2	2	2	2
TSH ^d	10	10	10	10
Leather waste (%wt)	0	14.3	25.1	33.44

^aPart per hundred parts of rubber by weight.

^bMBTS is dibenzothiazyl disulfide.

^cTMTD is tetra methyl thiuram disulfide.

^dTSH is toluenosulfohydrazina.

model MA880, in order to obtain short fibers and leather fiber granules.

A two-roll mill of Makintec—modelo 379 m was used to prepare the composites. Firstly, natural rubber was milled with the leather shavings (friction of 1 : 1.25 at 65°C); then stearic acid was used as a co-activator, added and mixed for 5 min. After that, zinc oxide was added and mixed for 7 min as an activator to enhance the action of organic accelerators. MBTS, dibenzothiazyl disulfide, TMTD, and tetra methyl thiuram disulfide were added as accelerators and mixed for 3 min. Sulfur, which acts as a vulcanizing agent, was added and mixed for 5 min. TSH, toluenosulfohydrazina, a blowing agent, was added and mixed for 5 min. The quantities of the reagents are shown in Table III (experimentally defined).

The compounds were vulcanized and foamed via heat transfer process in an electrically heated hydraulic press to mold into microcellular rubber foam; this process involved a simultaneous curing and foaming at 125°C for 7 min. These conditions were based on a rheometric test of τ_{90} .

Characterization

The cyclic compression tests were carried out using the specimens taken with a 1.5 cm of radius and 1.0 cm of edge, and they were submitted to five compression–decompression cycles at 70% of their original height and velocity of 100 mm/min, according to ISO 3386-1:1986.²² For the SEM analysis a Digital Scanning Microscope DSM-960-ZEISS was used. The samples were cut in standard area (0.5 cm × 0.5 cm × 0.5 cm) and covered with gold. The samples were analyzed under ×40 and ×200 magnification.

Density measurements for the composites (after mixture of vulcanization and foams agents) were carried out evaluating the solid density (before the thermal treatment) and foam density (after the thermal treatment). The measurements were performed by geometric method, according ASTM D 1622-08.²³

Relative foam density, related to the efficiency of the expansion processes, was measured according to ASTM D 3577,²⁴ using

eq. (1) as follows (considering the density measurements according ASTM D 1622-08):

$$\text{Relative Density} = \frac{\text{foam density}}{\text{solid density}} \quad (1)$$

The foam density is relative to the composites after the expansion process (thermally), and the solid density is related to the density measured before the expansion process.

The cell density (N_v , number of cells per cubic centimeter of the solid material) was calculated by eq. (2).²⁵ This calculus is based on the Kumar's theoretical approximation. The cell density is calculated by using an image processing analysis tool based on the software Image J.²⁶

$$N_v = \frac{N_v}{1 - V_f} \quad (2)$$

where V_f is the volume fraction of voids (porosity) and N_v is the number of cells per cubic centimeter of the foamed material. These parameters are calculated by eqs. (3) and (4), respectively.

$$V_f = 1 - \frac{\rho_f}{\rho_s} \quad (3)$$

$$N_v = \left[\frac{(nM^2)}{A} \right]^{3/2} \quad (4)$$

In these equations, ρ_f/ρ_s is the relative density of the foamed material, n is the number of cells analyzed, A is the image area, and M is the magnification factor of the micrograph.

Differential scanning calorimetry (DSC) measurements were carried out in DSC from NETZCH 209 model. The samples of about 5 mg sealed in aluminum pans were heated from −100 to 500°C at a scanning rate of 10°C/min under nitrogen atmosphere.

Thermogravimetry (TG) curve and differential thermogravimetry (DTG) were carried out using TGA NETZCH 242C model. The samples of about 5 mg were placed in an alumina pan and they were heated from room temperature to 900°C with a heating rate of 10°C/min.

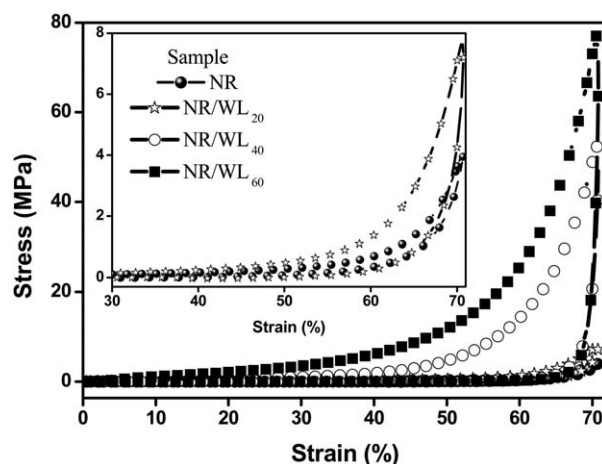


Figure 1. The first cyclic stress–strain in the case of compression until 70% compression of the original height according to ISO 3386-1:1986, for expanded rubber and for composites with 20, 40, and 60 phr of leather waste.

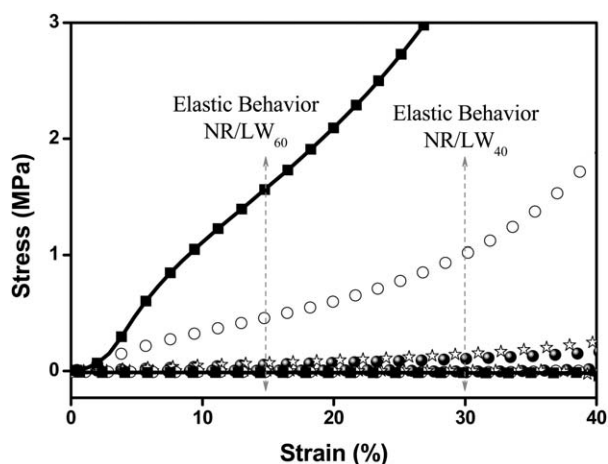


Figure 2. The cyclic stress–strain in the case of compression until 70% compression of the original height according to ISO 3386-1:1986 for 40 and 60 phr of leather waste (amplification on the viscoelastic behavior).

The chromium content in the composites was determined according to the NBR 10005/2004.²⁷

The strain–stress tests were performed in a universal testing machine EMIC model DL2000 at 500 mm/min with load cell of 5 kN using an intern deformation transducer. For this test, samples were prepared according to ASTM D-412 model C.²⁸

RESULTS AND DISCUSSION

Mechanical Properties Evaluation

Figure 1 represents the cyclic stress–strain curve in the case of compression at room temperature for all samples. The compression cycles were obtained until 70% compression. During the first cycle, the expanded rubber and the NR/LW₂₀ composite exhibited a viscoelasticity behavior (Figure 1 (inset)), while the samples with 40 and 60 phr of leather waste have similar behavior on a strain of about 15 and 30%, respectively (Figure 2). After the viscoelasticity strain, the NR/LW₄₀ and NR/LW₆₀ composites show viscoplasticity behavior and increase of hysteresis, i.e. the samples become harder due to cells compaction.

In cyclic compression, the structures absorb energy when compressive loads are applied and they release energy when the loads are removed. The hysteresis is defined as the energy lost in a cycle caused by the reconfiguration of the cells, the closing of cells during the compression molding as well as the opening of these cells when the compression is ceased.²⁹ The energy is

Table IV. Hysteresis Loop Area, Calculated by Measuring the Area Related to the Cyclic Compression Curves, for Expanded Rubber and for Composites with 20, 40, and 60 phr of Leather Waste

Sample	Hysteresis (MPa)
NR	0.126
NR/LW ₂₀	0.206
NR/LW ₄₀	3.459
NR/LW ₆₀	7.552

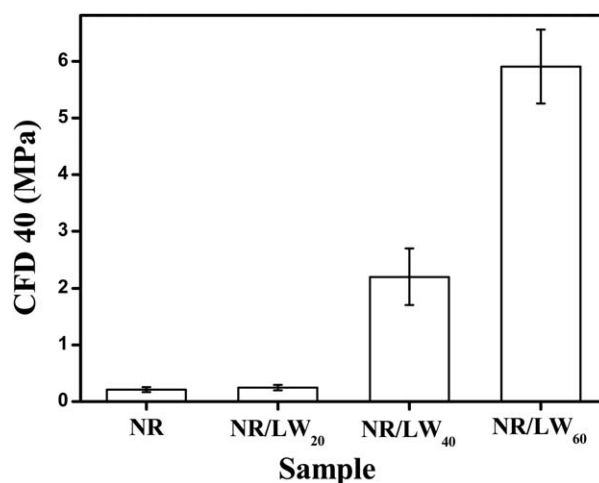


Figure 3. Compression force deflection at 40% compression, CFD 40, values obtained from the first cyclic of compression, for expanded rubber and for composites with 20, 40, and 60 phr of leather waste.

dissipated under compression and decompression processes produced in each cycle.³⁰

The measurement of hysteresis predicts possible deformations that will influence the flexibility of the foam. It was observed that when increasing the quantity of leather waste in the polymeric matrix, the hysteresis values increases (Table IV), which means that the system was losing its ability to return to the original shape.³¹ The loss of energy during the compression–decompression led to deformation of the matrix. The hysteresis values are calculated by measuring the area related to the cyclic compression curves. It could be attributed to the interfacial interaction between waste and natural rubber. This interaction would decrease the effectiveness of the stress transfer from rubber and consequently increase the work required to deform the composites, which leads to an increase in the Young's modulus.^{32,33}

Moreover, a relation between the density and the mechanical behavior could be established. According to Ismail *et al.*,³¹ who investigated foams produced with nitrile butadiene rubber NBR with different densities, the samples with the smallest density were more sensitive toward changes in strain energy and showed softer character. This behavior is similar to the foam studied in this article, in which the samples with the lowest density were more sensitive to strain energy and consequently, it was not necessary to make much effort to deform them.

Table V. Leached Concentration of Chromium (Cr) Based on the Limits Specified in the NBR1004 from Composites with 20, 40, and 60 phr Leather Waste

	Concentration (mg L ⁻¹)			
	NR/LW ₂₀	NR/LW ₄₀	NR/LW ₆₀	Limit of detection (NBR 1004/2004, annex F)
Chromium	0.74	1.39	3.88	5.0 mg/L (5 ppm)

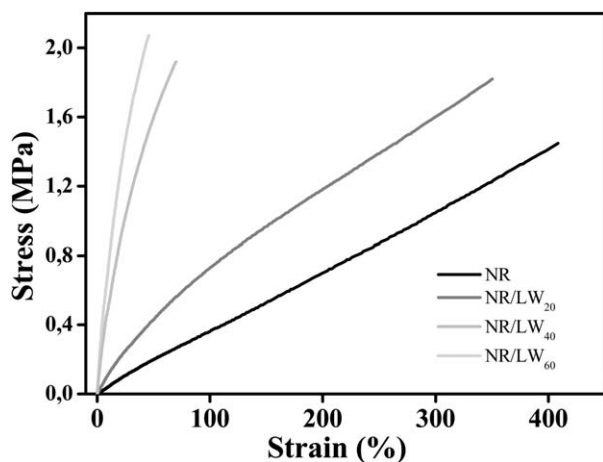


Figure 4. Mechanical properties stress–strain curve, obtained from the stress–strain test using a Universal Testing Machine-EMIC model DL2000 at 500 mm/min with load cell of 5 kN according to ASTM-D-412 of composites without leather waste (expanded NR) and composites with 20, 40, and 60 phr leather waste.

Another important parameter obtained in the mechanical analyses was the compression force deflection (CFD) at a 40% compression (values obtained from Figure 1 at 40% of deformation for the first cycles of compression). The foam was submitted to the necessary compression to cause a deformation of 40% of the original size. This parameter quantifies the compression that flexible foam supports without a significant loss in morphology. The higher the CFC 40 value, the more difficult the compression becomes because the foam is harder and therefore it has a greater dimensional stability. Figure 3 shows the graph obtained for CFD 40 as a function of different amounts of leather waste.³⁴

It was also noticed that the stiffness of the sample rises by increasing the concentration of the leather shavings, which improves the dimensional stability. However, the foam must have equilibrium between the CFD 40 and hysteresis. Despite the results that improved dimensional stability of the foam, the increase of filler favored the deformation of the composites. However, the preparation of the natural rubber/leather waste foam composite showed high mechanical properties and morphological structure (cells density), which classifies the composite as a new technological material, as shown in Table V the concentration of chromium released by leaching from leather composites are lower than the limits specified in the NBR 1004 (5.0 mg/L or 5 ppm). This proves that the composite could be used without any restriction.

Stress–strain tests were carried out comparing the mechanical properties of expanded rubber with the NR/LW composites for different amount of waste incorporated (Figure 4). The stress–strain results did not show an elastic deformation, which is common when evaluating natural rubber composites. This fact is attributed to the porous of the foam that causes internal tension points on the composites structures avoiding the flexibility of the polymeric chain. According to Figure 5, increasing the amount of leather waste increases the strength at rupture from 1.38 (expanded rubber) to 2.18 MPa (NR/WL₆₀), attributed to

the interfacial adhesion between the leather and rubber, i.e. the strength is transferred from the matrix to leather waste and therefore requires more stress to reach the rupture. The increase of strength (tension resistance) is characteristic of the leather waste that reinforces the structural chain of the rubber, i.e. working as filler on the structure of the polymer features. Nevertheless, the deformation at rupture decreases from natural rubber (408.7%) to 20 phr (394.9%) due to a reduction in the mobility of rubber chain attributed to the presence of the filler which increases the rigidity of the polymer (Young's modulus increased from 0.0026 MPa (expanded rubber) to 0.1206 MPa (NR/LW₆₀) according to Figure 6). Moreover, evaluating the composites of 40 and 60 phr of leather waste, the deformation at break is highly decreased, reaching 73.8 and 57.6% of deformation, respectively. These features could be related to the limit of leather incorporated, which represents the limit of leather embedded by the polymeric matrix. It can represent a challenge if the implementation of the foam requires high strain resistance. Therefore, decreases of the deformation did not represent failure since both the compression resistance and strength increases with the leather incorporation.^{35–38}

Morphological Evaluation and Cells Formation

The SEM micrographs of expanded rubber and the expanded composites with 20, 40, and 60 phr of leather waste are shown in Figure 7. In all samples it could be seen a high-quality of leather dispersion in the natural rubber, demonstrating physical adhesion, i.e., the leather is encapsulated by the natural rubber. The expansion process occurred in the natural rubber because of the decomposition of the blowing agent (toluenosulfohydrazine) which generates gases that exert pressure in the polymer, resulting in the formation of cells and consequently, expanding the material.

Figure 8 shows micrographs of the composites NR/WL₂₀ and NR/WL₆₀ before the expanding process to compare the changes in the cells. Smaller porous are observed and are attributed to the temperature reached during the mixing process. Therefore,

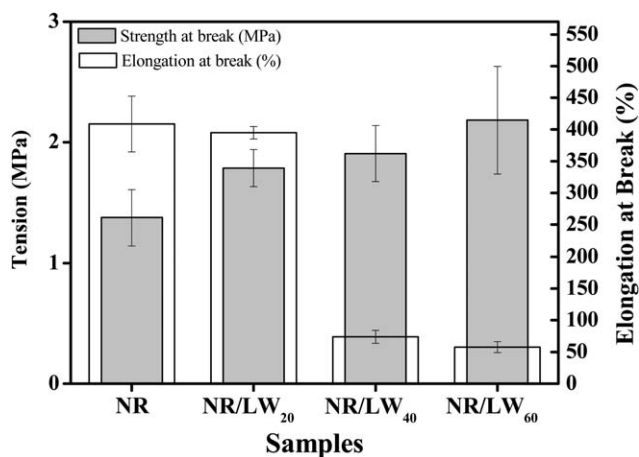


Figure 5. Mechanical properties (strain (MPa), elongation at break (%)) obtained from the stress–strain test using a Universal Testing Machine-EMIC model DL2000 at 500 mm/min with load cell of 5 kN according to ASTM-D-412 of composites without leather waste (expanded NR) and composites with 20, 40, and 60 phr leather waste.

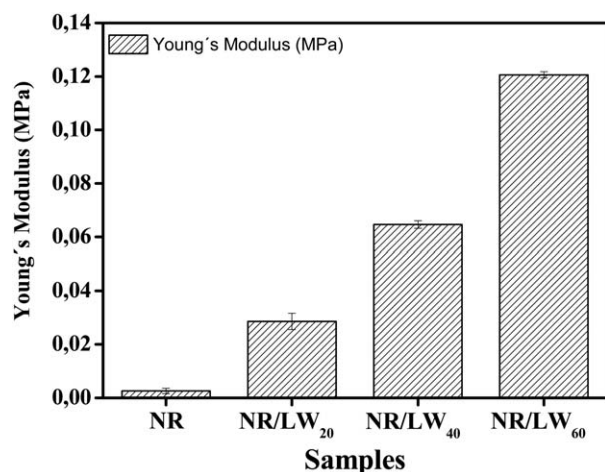


Figure 6. Mechanical properties, Young's Modulus (MPa), obtained from the stress-strain test using a Universal Testing Machine-EMIC model DL2000 at 500 mm/min with load cell of 5 kN according to ASTM-D-412 of composites without leather waste (expanded NR) and composites with 20, 40, and 60 phr leather waste.

it is possible to conclude that the expanding process enables the decomposition of the blowing agent with generation of cells even in the high concentration of leather.

Figure 9 shows the micrographs of the leather waste where a fibrous structure with different sizes was observed. Fibers of high diameters are formed by the interlacement of the smaller

fibers resulting in a material with flexibility and mechanical resistance.

The analyses of SEM images by the software (ImageJ) are shown in the frequency versus cell size graphic in Figure 10. The natural rubber foam cell is bigger than the composites with 20, 40, 60 phr of leather, which is higher than 1000 μm , corresponding to 75% of the total number of cells. The composite with 60 phr of leather has the smallest size of cell, between 100 and 400 μm , corresponding to 83% of total number of cells. The composites with 20 and 40 phr of leather waste present the largest variability in the distribution of cell size. Sizes between 100 and 400 μm are found in 57% of NR/LW₂₀ cells and 62% of cells from NR/LW₄₀ composites. Furthermore, cells sizes between 400 and 700 μm appear in 37% of cells from NR/LW₂₀ and 36% of cells from NR/LW₄₀ composites, respectively. The decrease in cell sizes with increase of leather waste is also notice evaluating the density of the composites after expansion process (thermal treatment), defined in Table VI as foam density.

The values of cell density (distribution) are shown in Table VII. The results reveal that the number of cells decreases by increasing the amount of leather waste from NR to NR/LW₂₀ and NR/LW₄₀, attributed to the decreasing on cells' sizes, as evaluated using SEM microscopy. The cell density measured for NR/LW₆₀ (25516.79 cell/cm³) is smaller than measured for NR foam (34004.89 cell/cm³). This result is attributed to higher strength resistance, reached by incorporation of 60 phr of leather waste, preventing the expansion process, i.e. generating smaller number/sizes of cells.

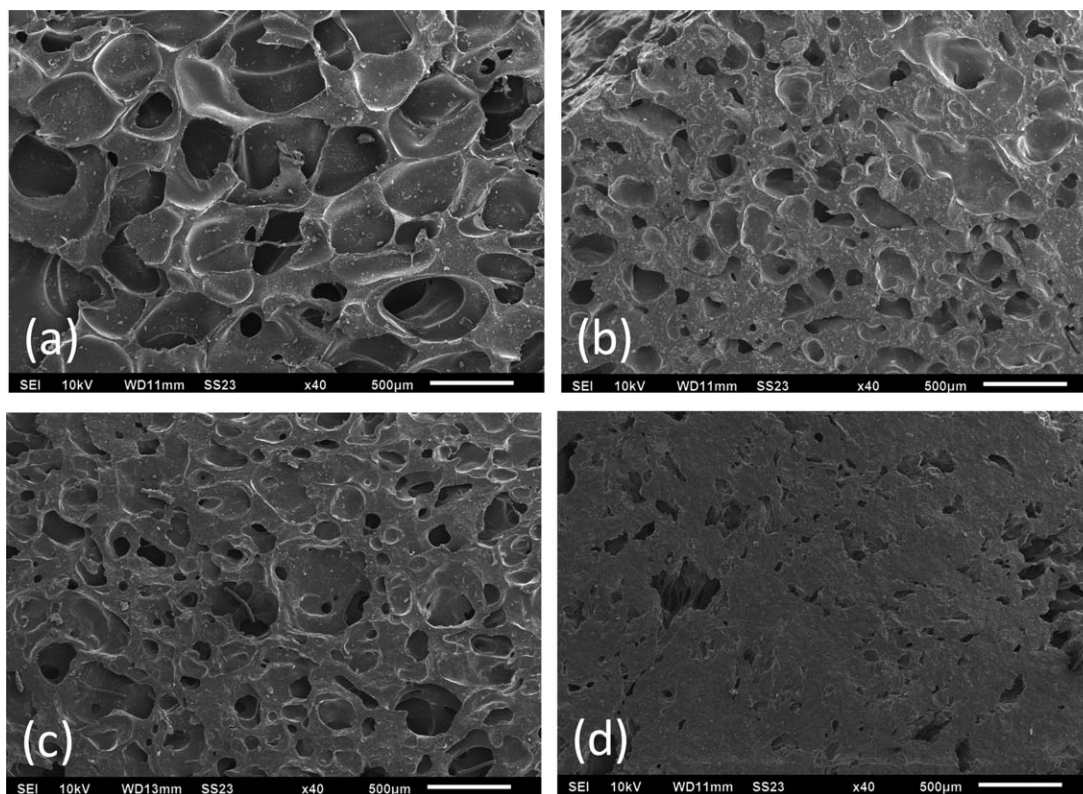


Figure 7. SEM micrograph using a digital scanning microscope, DSM-960-ZESS, of fracture surface: (a) expanded rubber, (b) composite with 20 phr of leather waste, (c) composite with 40 phr of leather waste, and (d) composite with 60 phr of leather waste.

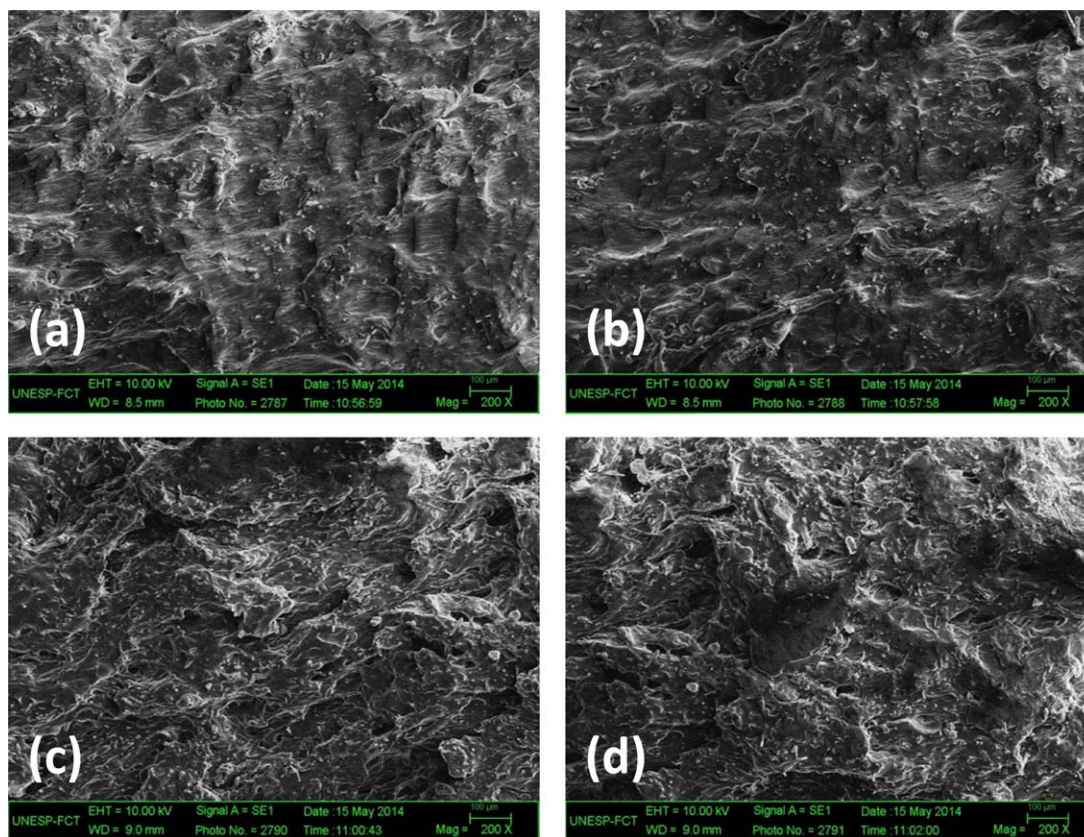


Figure 8. SEM micrograph of fracture surface, using a DSC-960-ZEISS: (a, b) composite NR/LW₂₀ before the expanding process, (c,d) composite NR/LW₆₀ before the expanding process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Moreover, the influence of leather in the expanding process is evident, increasing the relative density (Table VI), i.e. generating smaller cells as well as decreasing the degree of uniformity distribution on cells sizes with increases on leather concentrations. Moreover, the expansion process is evaluated through the difference on densities before (solid density) and after (foam density) the thermal expansion processes (Table VI).

The solid density (Table VI), i.e. the mixture of natural rubber, leather waste, and reagents compositions before the process of

thermal expansion, decreases in terms of increase in the amount of leather. It is attributed to the lower density (0.80 g/cm^3)³⁹ of leather waste when compared to molecular density of natural rubber (0.93 g/cm^3), which is dispersed on rubber matrix at higher concentrations per square meter when compared to the same composite's area (increasing the amount from 20 to 60 phr).

It is noticed that the $\delta\rho$ decreases with increases of leather amount as result of decreasing the efficiency of expansion

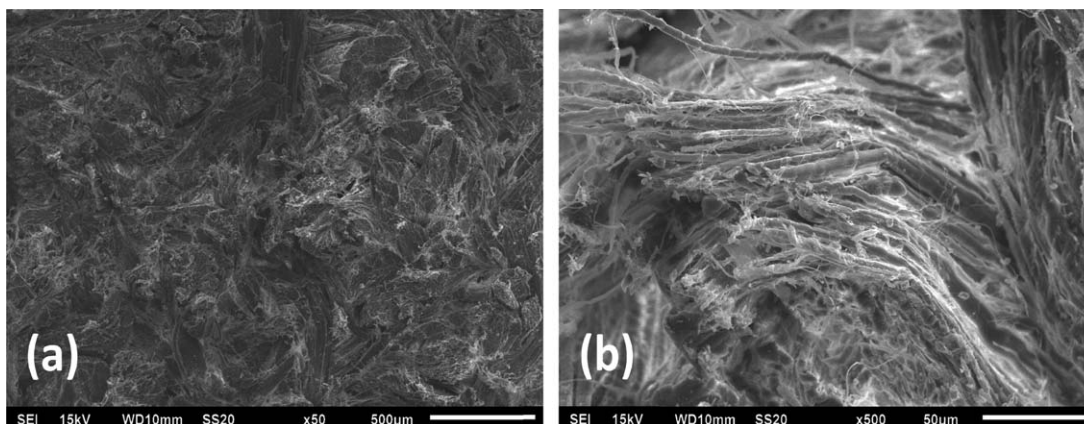


Figure 9. SEM micrograph using a digital scanning microscope, DSM-960-ZESS, of fracture surface: (a) leather waste 50 \times , (b) leather waste 500 \times .

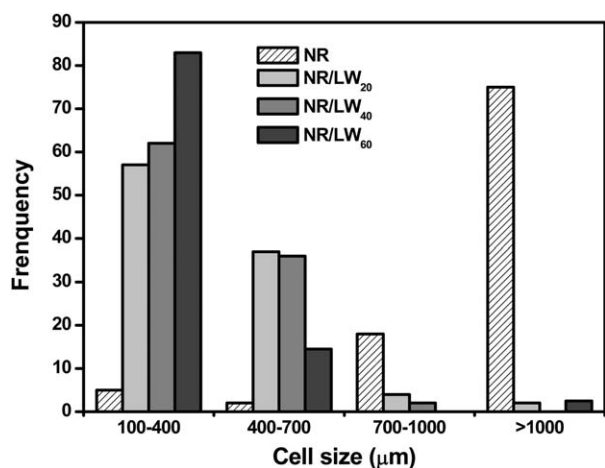


Figure 10. Graphic of frequency versus cell size rate, for expanded rubber and for composites with 20, 40, and 60 phr of leather waste.

process, decreasing the relation of cells number/sizes distribution on the composites.

Decreases on both cell density (number cells per square meter) as well as cells' sizes is mainly attributed to the leather waste (fibers) acting as fillers, i.e. reinforcing the polymeric matrix. The stress-strain resistance, supplied by leather waste composites, is mainly attributed to the response from leather fibers, requiring high intensity of stress to reach the deformation and consequently, the expansion process. The reinforcement process was previously discussed (according Figure 6), mainly noticed regarding the decreases on the Young's modulus generated by increases on leather waste amount incorporated. The process of rendering the cells growth and changes on the parameters of the cells (density and sizes) is commonly reported.⁴⁰ For instance, studies reported the influence of fillers which tend to modify the microstructure of PU foam, producing cells with smaller sizes as well as higher cell density.^{14,41-43} Similar results are reported by Shan *et al.*,⁴⁵ which shows the increase of coir fibers, inserted as fillers in composites, increases the mechanical strength hindering the expansion process.

Thermal Analyses

Figure 11 shows the DSC of the expanded rubber and the composites with 20, 40, and 60 phr of leather waste. It is observed an endothermic event around -68°C attributed to the glass transition (T_g) from rubbers, a property characterized by the transition of the glassy state to the viscoelastic without the occurrence of a structural change, i.e. the material loses stiffness (caused by freezing) and gain elastomeric properties. It was

Table VII. Cell Density (cell/cm^3) Calculated Using the Method Suggested by Kumar's, for Expanded Rubber and for Composites with 20, 40, and 60 phr of Leather Waste

Sample	Cell density (cell/cm^3)
NR	34,004.89
NR/LW ₂₀	89,785.85
NR/LW ₄₀	57,081.65
NR/LW ₆₀	25,516.79

also observed an exothermic peak around 378°C related to the degradation of polymeric chains that constitute the rubber and an endothermic peak around 420°C associated to a slow degradation of polymeric chains of higher weight.

Comparing the DSC curve of the composites with 20, 40, and 60 phr of leather to the expanded rubber, it was observed similar transitions characteristic of the natural rubber. In addition, the measurements have shown two main endothermic processes, the first one, around 86°C , is assigned to the dehydration of the collagen from leather.⁴⁴ The asymmetry of the DSC peak is due to presence of collagen populations with different hydrothermal stabilities. Thus, the sharp component of the peak is assigned to native collagen population, whereas the shoulder observed at higher temperatures is attributed to a more stable/stabilized collagen with a higher crosslinking degree.⁴⁵ The second endothermic process at above 200°C is related to the leather's denaturation, i.e. the main phase of leather degradation.^{46,47} It is important to emphasize that there is not any process related to the blowing agent, which proves that all of them were decomposed during the curing and expanding process.

Figure 12 shows the TG and Figure 12 (inset) shows the DTG from the expanded rubber and the composites with 20, 40, and 60 phr of leather waste. For the natural rubber, the main degradation processes between 270°C and 455°C (76% of mass loss) are attributed to the degradation of polymeric chains through crosslinking and chain scission, according to Figure 13. In the case of crosslinking a very small loss is associated with the formation of aldehydes, ketones, and carboxylic acids.⁴⁸

However, when analyzing the DTG curve, we observe the presence of a second stage of mass loss with maximum at 435°C (21.3% of mass loss), characteristic of slower degradation of the polymer chains of higher molecular weight. The residual mass from natural rubber was 2.7%. The results of NR/LW composites presented a first degradation stage around 64°C attributed to the release of water, similar to the natural rubber without

Table VI. Values of Real Density Measured According to ASTM D 1622, Relative Density Measured According to ASTM D 3577, and $\Delta\rho$ (Solid Density—Foam Density), for Expanded Rubber and for Composites with 20, 40, and 60 phr of Leather Waste

Sample	$P(\text{solid density})$ (kg/m^3)	ρ_{Real} (foam density) (kg/m^3)	$\Delta\rho$ (Solid density—Foam density)
NR	930.0	470.7	459.3
NR/LW ₂₀	905.0	558.8	346.2
NR/LW ₄₀	888.0	670.4	217.6
NR/LW ₆₀	876.0	848.6	27.4

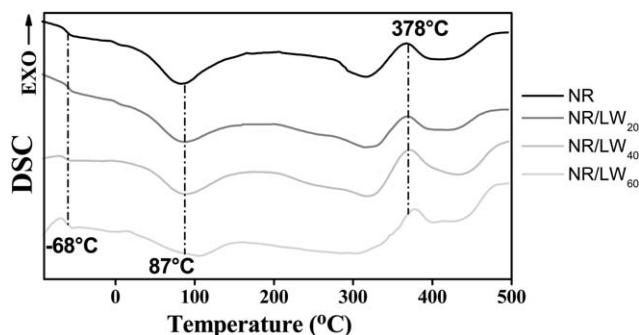


Figure 11. DSC curve, obtained using a DSC from NETZCH 2099 model, the sample of about 5 mg were heated from -100 to 500°C at a scanning rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere, for the expanded rubber and the composites with 20, 40, and 60 phr of leather.

leather waste. The second stage starts at about 268°C and finishes at 450°C and is related to the polymeric chain degradation from natural rubber as well as the cleavage of collagen bonds from leather waste and corresponding to the decomposition into CO_2 as well as some NO_x species, with a mass loss around 70%,^{44,49,50} reaching 71.9, 70.0, and 64.3% of mass loss to 20, 40, and 60 phr of leather waste incorporated, respectively.⁵¹ Moreover, the mass loss decreases by raising the amount of leather waste incorporated into composites. This mass loss is related to the third step observed in the thermogravimetry curve. The processes that occur between 450 and 658°C are attributed to the degradation of leather tanning agents with 17.2% of mass loss for NR/LW₂₀, 16.9% of mass loss for NR/LW₄₀, and 15.8% of mass loss of NR/LW₆₀. Residual mass associated to the inorganic materials, e.g. chromium and curing agents, increased around 6.2, 8.1, and 15.8% for the composites with 20, 40, and 60 phr of leather waste, respectively. Finally, the increase in the amount of leather waste incorporated in the rubber composites enhanced the thermal resistance when compared to the rubber.

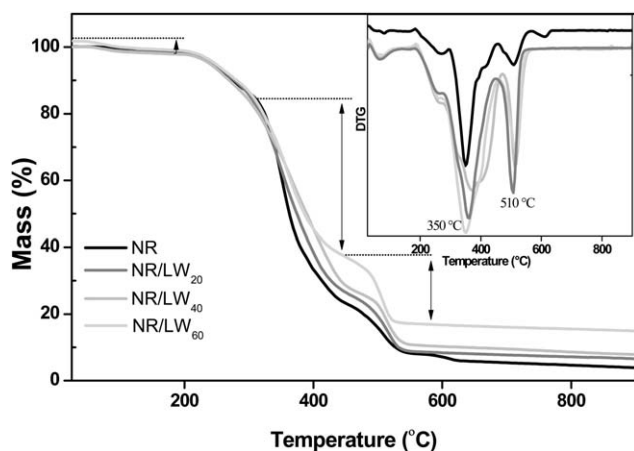


Figure 12. TG curve, obtained using a TGA from NETZCH 242c model, the sample of about 5 mg were heated from room temperature to 900°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere for the expanded rubber and the composites with 20, 40, and 60 phr of leather.

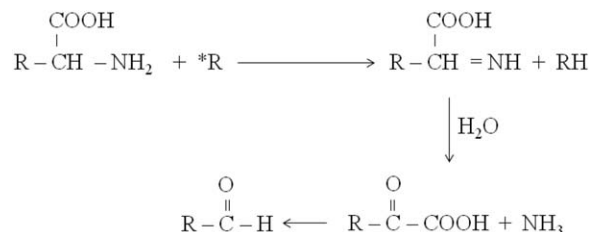


Figure 13. Crosslinking of polymeric chains associated with the formation of aldehydes, ketones, and carboxylic acids.

CONCLUSIONS

The effect caused by incorporating leather waste on natural rubber to produce an expanded composite is related to the amount of leather in the mixture, which influences directly on cells structure and on mechanical properties. The cell structure was analyzed by microscopy and the results showed that the leather shavings tend to hamper the expanded process, resulting in smaller and fairly uniform cells, which define different densities for the composites. The mechanical properties were investigated and the composites exhibited a great strength and energy absorption capacity. The increase of leather shavings on the mixture improves the hardness of the composite, elevating the necessary force to strengthen the composite. Therefore, it is possible to produce composites with leather waste with different characteristics that can be directed to many applications according to foam density and the hardness required.

ACKNOWLEDGMENTS

The authors acknowledge EMBRAPA Instrumentações and Universidad de Valladolid for providing the experimental data.

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