

An Innovative Material Based on Natural Rubber and Leather Tannery Waste to Be Applied as Antistatic Flooring

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ABSTRACT: In recent decades, the production chain of beef and bovine leather has grown significantly because of an increase in the world's population and improved access to consumption. However, the generation of waste derived from this sector has grown simultaneously, and consequently, improved ways of adding value, reusing, and disposing these waste materials are being sought. In this article, we present a new and innovative composite material based on vulcanized natural rubber (NR), carbon black (CB), and leather waste (NR/CB/leather). The NR/CB/leather composites were prepared by thermal compression with 60 phr of CB and 60 or 80 phr of leather waste. In accordance with Brazilian sanitary laws, we exposed these composites for 24 h to bleach (B) and a disinfectant with the aim of simulating a true everyday cleaning use. The deconvolution of the impedance semicircles was carried out, and two relaxation phenomena around linear relaxation frequencies of about 10^5 and 10^6 Hz were found and associated mainly with charge carriers from CB and leather waste. With the addition of leather, the electrical conductivity of the composites increased two orders of magnitude from 5.70×10^{-6} for the NR/CB to 7.97×10^{-4} S/cm for NR/CB/leather-60 phr B. These results point to the possibility of using these composites as an antistatic flooring once they exhibit acceptable values of electrical conductivity and once they withstand, from the structural, morphological, and electrical point of view, exposure to sanitizing agents. Furthermore, the production of these composites will add value to and enable an environmentally acceptable disposal of leather waste. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41297.

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INTRODUCTION

The growth of the world's population demands a substantial increase in the consumption of natural resources and manufactured products; this implies the generation of significant quantities of solid waste. Currently, it is known that only a small portion of the solid waste generated is recycled, and the other part, especially industrial waste, is directed to sanitary landfills. This causes economic losses and environmental impact.¹ Considering this situation, research groups in science and rubber technology are directing their efforts to the development of biodegradable, biocompatible, and recyclable materials; the reduction of the extraction of natural resources; the addition of value to the waste itself and the production chain that originated the waste.²

Because of natural rubber's (NR's) distinctive ability to incorporate large amounts, up to 120 phr, of solid and inert particles,

which helps it maintain acceptable mechanical properties, it is an excellent choice of polymeric matrix for the generation of new recycled materials. For instance, in the last few years, (1) peanut shell powders were used as fillers in NR with excellent results as far as the mechanical properties were concerned,³ (2) rice husk ash was used as a filler in high-density polyethylene to improve its tensile strength,⁴ and (3) micronized tire waste was used as an inert filler in cement production⁵ and for the manufacture of floating support plant pots.⁶

Because of the complexity of the leather tanning process, a huge variety of waste is available for recycling; this includes buffing, stripping, and shaving wastes. Data from a Brazilian tannery in Presidente Prudente/São Paulo State or San Paul State (SP) in 2013 showed that for every 3000 pieces of leather produced in a day, a volume equal to 19 m^3 of waste is produced, and the total cost for its removal and disposal to landfills is about

Table I. List of Components and Their Receptivity Quantities for the NR/CB, NR/CB/Leather-60 phr, and NR/CB/Leather-80 phr Composites

Component	Quantity (phr ^a)
Base formulation	
Dry NR	100
Leather waste	60 and 80
CB	60
Vulcanization system	
Sulfur	2.5
Zinc oxide	5
Stearic acid	3
ZMB-2	1
Acceleration system	
MBTS	1.2
TMTD	0.4

^aphr, parts per hundred of rubber.

US\$500 per day because of the fact that leather waste has, on average, 3.5% trivalent chromium (Cr⁺³) and, depending on the environmental conditions, can result in the production of hexavalent chromium (Cr⁺⁶), which has a high potential to cause skin disease and can cause several kinds of cancer.^{7,8}

Leather waste can be used as an inert filler for the manufacture of polymeric composites with NR (*Hevea brasiliensis*) as the matrix. To improve the thermal and mechanical properties of the composites, a vulcanization process is required. Other active fillers, such as carbon black (CB),⁹ can be used with the aim of improving the electrical conductivity (σ), mechanical properties, and abrasion resistance and directing the material to a technological application, such as environmentally friendly and low-cost antistatic flooring. However, because of the complexity of a composite based on NR, CB, and leather waste, reports about this subject are not very abundant in the scientific literature.

In this article, we present a new and innovative composite material based on vulcanized NR, CB, and leather waste with potential for application in the area of antistatic flooring and provide a new, adequate, and environmentally friendly option for the disposal of leather waste, which is rich in chromium. The structural, morphological, and electrical characterizations of these composites before and after their exposure to sanitizing agents were carried out, and the results were analyzed with respect to the leather waste added and also with respect to the different quantities of waste that were added.

EXPERIMENTAL

Materials for the NR/CB–Leather Composites

Base Material. Dry NR (*cis*-1,4-polyisoprene) of the commercial variety CCB (Crepe Claro Brasileiro), financed by the DLP Industria e Comércio de Borracha e Artefatos in the city of Poloni/SP, was used for the preparation of the composites. This rubber is obtained in processing plants by the coagulation of latex from the *H. brasiliensis* species (clones RRIM 600). The starting reagents, with their chemical formulas, purities, and ori-

gins of the base formulation, vulcanization, and acceleration systems, used were as follows: zinc oxide (ZnO, 81.38 g/mol, analytical purity, VETEC), stearic acid [CH₃(CH₂)₁₆COOH, 284.48 g/mol, analytical purity, VETEC], sulfur (S₈, 256.52 g/mol, analytical purity, VETEC), methyl-2-methylmercaptobenzimidazole zinc salt (ZMB-2; C₁₆H₁₆N₄S₂Zn, 391.38 g/mol, $\geq 96\%$, LANXESS Energizing Chemistry), 2,2-dibenzothiazyl disulfide (MBTS; C₁₄H₈N₂S₄, 332.47 g/mol, $\geq 98\%$, LANXESS Energizing Chemistry), and tetramethylthiuram disulfide {TMTD; [(CH₃)₂NCS₂]₂, 240.43 g/mol, $\geq 94\%$, LANXESS Energizing Chemistry}.

CB. The CB used to produce the composites was N-330 with a purity greater than 99% and financed by Columbia Petroleum Industry. This kind of CB exhibits a density equal to 1.8 g/cm³, a superficial area between 70 and 99 m²/g, and an iodine index of 90 g/Kg. CB N-330 is widely used as a reinforcing agent for high-performance rubbers, radial tires, bias tires, conductive polymers, and other high-quality rubber products.

Leather Waste. The leather waste used for the preparation of the composites originated from the tanning process with basic chromium sulfate (CrOHSO₄), and it was formed mainly of buffing, stripping, and shaving wastes. The tanning process was responsible for providing the mechanical properties and degradation stabilities to the material. The leather waste was financed by the Vitapelli Tannery in the city of Presidente Prudente/SP, Brazil. These materials were micronized, and their pH was maintained at 3.5 during processing. The composite formulations are listed in Table I.

Preparation of the NR/CB–Leather Composites

The processing of the NR formulations was carried out in an open mixing mill or a rubber mixer (Makintec, model 379 m) for 20 min at 40°C in accordance with the ASTM D 3182 standard method.¹⁰ The composites were made with CB (60 phr), leather waste (60 or 80 phr), a vulcanization system consisting of zinc oxide (5 phr) and stearic acid (3 phr), which reacted with each other to form zinc stearate [2(C₁₇H₃₅COOH) + ZnO → (C₁₇H₃₅COO⁻)₂Zn²⁺ + H₂O], sulfur (2.5 phr), and ZMB-2 (1 phr), and an accelerating system consisting of MBTS (1.2 phr) and TMTD (0.4 phr). All of the quantities were mixed as noted in Table I. After undergoing two mixing processes, the formulations were compression-molded at 150°C with a closing pressure of 7.5 ton in a pneumatic press for 3'18", 3'43" and 4'34" for the NR/CB, NR/CB/leather-60 phr, and NR/CB/leather-80 phr, respectively. These time parameters were obtained previously from rheological assays. At the end of process, the following samples were prepared: NR/CB, NR/CB/leather-60 phr, and NR/CB/leather-80 phr. Similar processing techniques have been reported.^{11,12}

Exposure of the Composites to Sanitizing Agents: Bleach (B) and Disinfectant (D)

In accordance with the ordinance numbers 15¹³ and 89¹⁴ from the Brazilian Health Surveillance Agency (Agência Nacional de Vigilância Sanitária, ANVISA), which is an indirect administration agency of the Brazilian Ministry of Health (Ministério da Saúde, MS), and to ensure the potential use of composites as a floor covering, the samples were exposed at room temperature for 24 h to B and a D, products traditionally used for cleaning. Figure 1 shows the NR/CB/leather composites exposed to B (a)

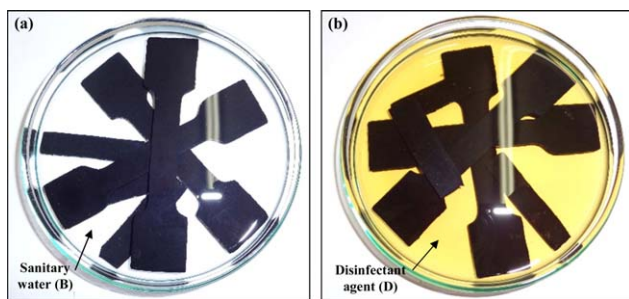


Figure 1. NR/CB/leather composites exposed to (a) B and (b) D at room temperature for 24 h in accordance with ordinances numbers 15 (August 15, 1988) and 89 (August 25, 1994) from the Brazilian Health Surveillance Agency Agência Nacional de Vigilância Sanitária (ANVISA), which is an indirect administration agency of the Brazilian Ministry of Health Ministério da Saúde (MS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and D (b). The main composition of D included *ortho*-benzyl-*p*-chlorophenol (0.25%), *ortho*-phenyl phenol (0.50%), formaldehyde, soap, pine oil, solvent, stabilizer, and water. The main composition of the B was sodium hypochlorite, active chlorine between 2.0 and 2.5% w/w, and water. At the end of the exposure process, the following samples were prepared: NR/CB/leather-60 phr B, NR/CB/leather-60 phr D, NR/CB/leather-80 phr B, and NR/CB/leather-80 phr D. The schematic representation of the general preparation process for the composites is shown in Figure 2.

Structural Characterization

The structural characterization of the composites was carried out by Fourier transform infrared (FTIR) absorption spectroscopy. The FTIR spectrophotometer used was a Bruker model Vector 22 in the region of 4000–700 cm^{-1} with an accuracy of 2 cm^{-1} and 128 scans. The attenuated total reflectance technique was used to examine the composite surface directly.

Morphological Characterization

The morphological characterization of the composites was studied with a Carl Zeiss scanning electron microscope (model EVO LS15) and energy-dispersive X-ray spectroscopy (EDX) with an EDAX Genesis. The composite measurements were performed directly on the metalized surface (100 \times) and the fractured surface (5000 \times) of the samples.

Electrical Characterization

Direct-current (dc) and alternating-current (ac) electrical measurements were carried out on the composites at room temperature and in atmospheric air. Gold electrodes with an area equal to 0.28 cm^2 were deposited on both faces of the samples by an evaporation technique in a vacuum at 10^{-6} mbar. The dc electrical measurements were carried out with a Keithley electrometer (model 6517A) in the voltage range from -3 V to 3 V. The data were plotted with the Cartesian plane formalism, voltage (V) versus inductance (I), and σ can be represented by the following equation:

$$\sigma = (RA)^{-1} \quad (1)$$

where R is the electrical resistance of the material and Λ is the geometric factor of the sample holder. In this case, the sample holder was similar to a parallel-plate capacitor, and $\Lambda = A/L$,

where A is the area of the metalized electrodes and L is the thickness of the sample.

The ac electrical measurements were carried out by impedance spectroscopy in the frequency range from 0.1 Hz to 1 MHz with an applied potential of 100 mV with an impedance analyzer (Solartron model SI1260) with a coupled dielectric interface (model 1296). The impedance data were plotted on Nyquist diagrams and normalized to a geometrical factor equal to unity. The data were plotted with the complex plane formalism, real part of impedance ($Z'(\omega)$) versus imaginary part of impedance ($Z''(\omega)$), and analyzes with Boukamp's EQUIVCRT software.¹⁵ This program works in an environment developed for equivalent electrical circuits based on the fitting of the emittance spectral data.¹⁵ The impedance [$Z^*(\omega)$] of a complex system is the apparent response formed by the contribution of all of the electrical active components of the system, and $Z^*(\omega)$ can be represented by the following equations:

$$Z^*(\omega) = \sum_i^n Z_i^*(\omega) = Z_1^*(\omega) + Z_2^*(\omega) + \dots + Z_n^*(\omega) \quad (2)$$

$$Z^*(\omega) = \sum_i^n \text{Re}_i(Z^*) + j \sum_i^n \text{Im}_i(Z^*) = \sum_i^n Z_i'(\omega) + j \sum_i^n Z_i''(\omega) \quad (3)$$

where n represents the number of electrically active components in the system.

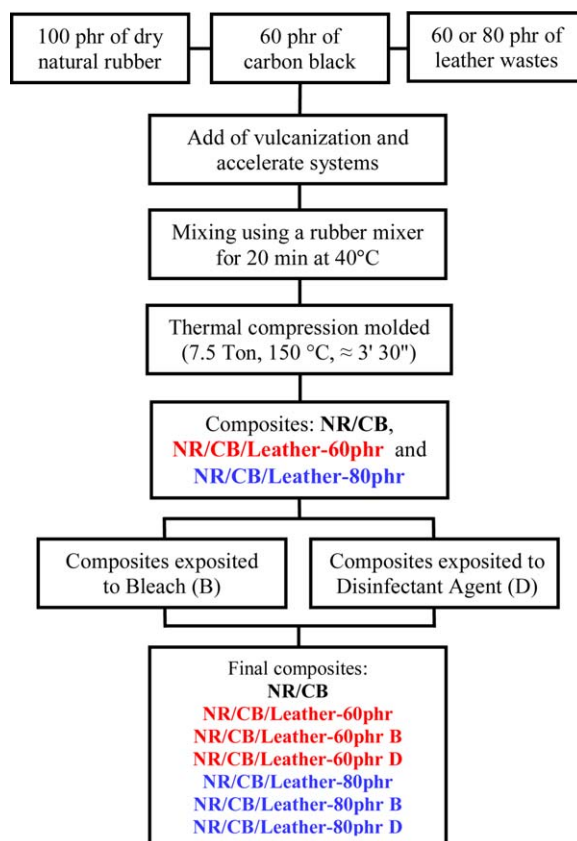


Figure 2. Flow-chart for the fabrication of the NR/CB, NR/CB/leather-60 phr, and NR/CB/leather-80 phr composites from the exposure stage to the sanitizing agents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. List of the Values of the Mechanical Parameters of the Composites Based on Vulcanized NR, CB, and Leather Waste

Composite	Stress-strain test		Compression test		Abrasion test (mm ³ /40 m)	Hardness Shore A
	ϵ_{MAX} (%)	σ_{MAX} (MPa)	ϵ_{MAX} (%)	σ_{MAX} (MPa)		
NR/CB	759.2 ± 19.1	18.6 ± 1.1	—	—	77.1 ± 4.1	42.0 ± 1.6
NR/CB/leather-60 phr	84.3 ± 1.6	12.2 ± 1.1	27.5 ± 1.0	12.6 ± 1.3	213.0 ± 11.9	72.7 ± 0.9
NR/CB/leather-60 phr B	113.0 ± 3.3	7.2 ± 0.6	—	—	230.5 ± 2.4	73.0 ± 0.8
NR/CB/leather-60 phr D	127.2 ± 2.1	6.6 ± 0.9	—	—	218.5 ± 1.8	73.7 ± 0.5
NR/CB/leather-80 phr	44.6 ± 1.0	8.6 ± 0.8	22.3 ± 0.1	18.0 ± 0.5	178.9 ± 3.3	76.0 ± 1.7
NR/CB/leather-80 phr B	32.9 ± 0.6	8.2 ± 0.2	—	—	181.9 ± 0.9	75.0 ± 0.8
NR/CB/leather-80 phr D	44. ± 2.4	7.7 ± 0.1	—	—	179.7 ± 1.1	75.2 ± 1.4

ϵ_{MAX} , maximum elongation; σ_{MAX} , maximum tensile.

The impedance of the NR/CB/leather composites [$Z_C^*(\omega)$] can be represented fundamentally by the following equations:

$$Z_C^*(\omega) = Z_{\text{NR}}^*(\omega) + Z_{\text{CB}}^*(\omega) + Z_L^*(\omega) \quad (4)$$

$$Z_C^*(\omega) = \left[Z'_{\text{NR}}(\omega) + Z'_{\text{CB}}(\omega) + Z'_L(\omega) \right] + j \left[Z''_{\text{NR}}(\omega) + Z''_{\text{CB}}(\omega) + Z''_L(\omega) \right] \quad (5)$$

where the subscripts NR, CB, and L are the contributions of NR, CB, and the leather waste, respectively.

Each impedance component or relaxation phenomenon in the system can have its electrical response represented by an equivalent electrical circuit (EEC) at zero frequency (constant field) and decomposed in elements of R , capacitance (C), I , and n , which represents the relaxation time (τ_0) distribution present in the system. When the n value is close to zero, the experimental data can be adjusted with the classical Debye formalism.¹⁶ This kind of formalism is in general used for simple systems, such as liquids and monophase ceramics. However, if the n value is different from zero, the most common formalism used is the Cole–Cole formalism,¹⁷ and the n parameter is related to the decentralization angle (α) of the semicircle by eq. (6):

$$n = \frac{2\alpha}{\pi} \quad (6)$$

With the R and C electrical elements estimated by simulation with EEC, it is possible to determine the linear relaxation frequency (f_0)/angular relaxation frequency (ω_0) coupled with τ_0 associated with the dipole system or dielectric relaxation process. f_0 , ω_0 , and τ_0 can be estimated by eq. (7):

$$f_0 = \frac{\omega_0}{2\pi} = \frac{1}{2\pi\tau_0} = \frac{1}{2\pi RC} \quad (7)$$

Mechanical and Structural Characterization

Considering that the NR/CB/leather composites had to exhibit appreciable mechanical properties and could not release toxic elements when used as flooring, stress-strain (ASTM 412), compression (ASTM 695), abrasion (DIN 53516), Shore A hardness (ASTM 2240), leaching (NBR 10005:2004), and solubilization (NBR 10006:2004) tests were

carried out, and a summary of these results is presented in Tables II and III.

RESULTS AND DISCUSSION

Morphological and Structural Characterization

Spectroscopic techniques, such as FTIR spectroscopy, are analytical techniques used for identifying specific bonds, elements, and structures in samples. FTIR spectroscopy is a very common technique because of the accuracy and quickness of the measurement. Figure 3 shows the IR absorption spectra between 4000 and 700 cm^{-1} for the NR/CB, NR/CB/leather-60 phr and NR/CB/leather-80 phr composites, whereas Table IV lists the tentative attribution of the bonds. As shown in the IR analysis [Figure 3(a) and Table IV], all of the spectra exhibited all of the vibration band characteristics of the poly(*cis*-1,4-isoprene) structure. It was possible to identify the presence of two main sets of bonds attributed to NR independently of the addition of CB and leather waste. The first set was around 3000 cm^{-1} , and the second set was around 1500 cm^{-1} . The principal attributions for the NR^{18,19} were a band at 3363 cm^{-1} attributed to the O–H stretching vibrations present in nonrubbers, this CB, leather waste, and vulcanized systems. The band at 2951 cm^{-1} was associated with a stretching band of C–H in olefin carbon. In the region of 2916 and 2847 cm^{-1} , the asymmetric and symmetric stretching of the methyl group (CH_3) occurred. At a frequency of 1534 cm^{-1} , the stretching band of C=C could be seen. The asymmetric and symmetric angular bending of the methyl group (CH_3) occurred in the region of 1442 and 1396 cm^{-1} . The band at 822 cm^{-1} was attributed to the twist of the C–H link in olefin. This band was typical of crosslinking in isoprene rubbers. Asymmetric C–S group stretching vibrations located at 567 cm^{-1} associated with the sulfur of the vulcanization system was expected. The principal attributions for the CB^{20,21} were bands at 2916, 2847, and 1635/1590 cm^{-1} , which overlapped with some NR bands, and were ascribed to asymmetric and symmetric stretching vibrations of CH in CH_2 and CH_3 and were attributable to highly conjugated CO in a quinone configuration, respectively. The principal attributions for the leather waste^{22,23} were at 2916 and 2847 cm^{-1} , which were the asymmetric and symmetric stretching bands of CH_2 . The band at 1635 corresponded to C=O of the amide group,

Table III. List of the Values of the Structural Parameters of the Composites Based on Vulcanized NR, CB, and Leather Waste

Test	Composite	NR/CB/leather-60 phr		NR/CB/leather-80 phr	
		Concentration (mg/L)	MVP (mg/L)	Concentration (mg/L)	MVP (mg/L)
Leaching	Arsenic	0.30 ± 0.01	1.0	0.50 ± 0.01	1.0
	Barium	27.8 ± 1.04	70	32.0 ± 1.26	70
	Cadmium	nd	0.5	nd	0.5
	Lead	0.06 ± 0.01	1.0	0.08 ± 0.00	1.0
	Chrome	0.6 ± 0.02	5.0	0.80 ± 0.02	5.0
	Mercury	nd	0.1	nd	0.1
	Silver	0.01 ± 0.00	5.0	0.01 ± 0.00	5.0
	Selenium	nd	1.0	nd	1.0
	Solubilization	Aluminum	0.10 ± 0.01	0.20	0.15 ± 0.01
Arsenic		nd	0.01	nd	0.01
Barium		0.18 ± 0.05	0.70	0.21 ± 0.02	0.70
Cadmium		nd	0.00	nd	0.00
Lead		nd	0.05	nd	0.05
Copper		0.01 ± 0.00	2.00	0.02 ± 0.00	2.00
Chrome		0.01 ± 0.00	0.05	0.02 ± 0.00	0.05
Iron		0.02 ± 0.00	0.30	0.04 ± 0.00	0.30
Manganese		0.04 ± 0.00	0.10	0.05 ± 0.00	0.10
Mercury		nd	0.001	nd	0.001
Silver		nd	0.01	nd	0.01
Selenium		nd	0.05	nd	0.05
Sodium		74.50 ± 2.36	200.00	87.40 ± 3.49	200.00

MVP, maximum value permitted; nd, not detected.

and the band at 1537 corresponded to the NH bending of amino acids. Weak bands attributed to the leather waste were found below 1250 cm^{-1} , and they corresponded to the $-\text{CN}$ and $-\text{CO}$ groups of leather amino acids. As shown in Figure 3, the addition of CB and leather waste did not significantly modify the IR spectrum and the vibration bands of the NR. This observation was indicative of a low chemical interaction of the fillers with the polymer matrix. Moreover, because of the compatibility in the NR/CB/leather, it was possible to obtain volumetric homogeneous composites, as shown by the scanning electron microscopy (SEM) pictures. As required, the exposure of the composites to both B and D did not cause a significant structural alteration in the composites; this indicated that from a structural point of view, the composites could be applied as floor covering materials.

Because of its high magnification and resolution, SEM is a useful tool for revealing information, such as the superficial and volumetric morphologies and homogeneities, anisotropies, and textures of the samples. Figure 4 shows the SEM images and EDX spectra at room temperature of the metalized surface with a magnification of $100\times$ and the fractured surface with a magnification of $5000\times$ of the NR/CB, NR/CB/leather-60 phr, and NR/CB/leather-80 phr composites. As shown in Figure 4, a satisfactory superficial and volumetric homogeneity was observed; this indicated an efficient mixing process and its appropriate

quantities, types of curing system, vulcanization conditions for preparing nanocomposites, and satisfactory compatibility between NR, CB, and mainly leather waste. This satisfactory compatibility was attributed principally to the large quantity of superficial charges and the reactivity of the CB and leather waste. There were some white points on the surface of the composites, and three representative white points are indicated by the arrows in Figure 4(a) for both magnifications. These points were associated with CB and the vulcanization system, in particular, zinc and sulfur on a submicrometric scale. This fact was already verified with X-ray diffraction tests by Bellucci et al.¹² in a similar system. For Figure 4(b,c), it was possible to identify white points on the surface of the composites, and three representative white points were indicated by arrows. In this case, the points were associated with particles of the vulcanization system, CB, and leather particles. Visually, different textures for the composites could be seen with leather waste because of their fibrous structure. This same fibrous structure became more evident in the images of the fractured surface [Figure 4(b,c) on right] in which the fibrous structure and small holes could be seen because of the weak interfacial adhesion between the leather fibers and polymeric matrix. As required, the exposure of the composites to both sanitizing agents (B and D) did not cause a significant morphological alteration in the composites, and for this reason, these SEM images were omitted. In the EDX spectra, peaks of C, O, S, and Zn were identified and

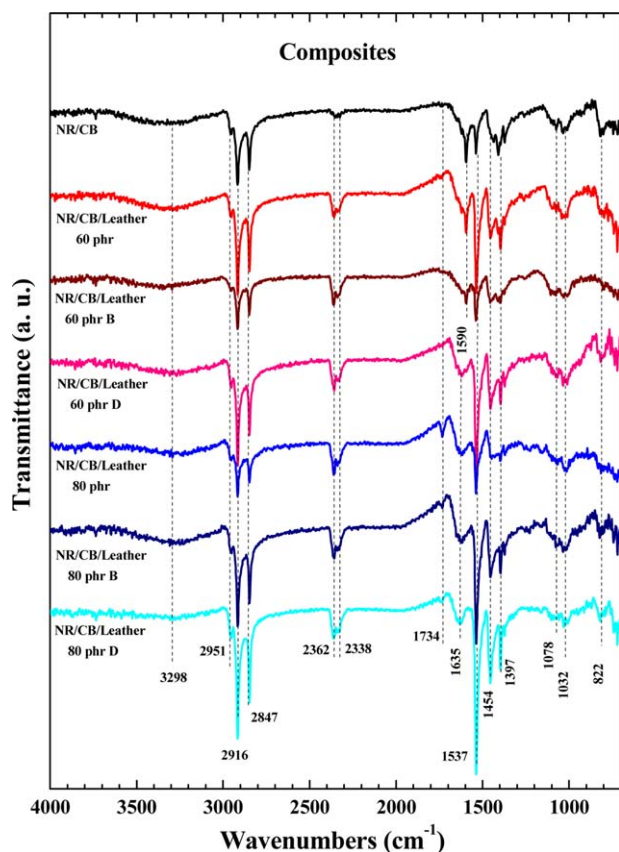


Figure 3. IR spectra at room temperature of the NR/CB, NR/CB/leather-60 phr, and NR/CB/leather-80 phr composites. In detail, the maximum frequency values for the main characteristic bands are shown. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

associated with the polymer chain, CB, and curing system. The percentage differences observed with the EDX spectra for the S and Zn elements in the composites referred only to the part of the sample investigated and the time of exposition of the sample to the X-ray. The peak of Au was associated with the metalization process, and the low percentages of Na, Al, Si, Cl, K, Ca, Fe, and Zn were found for samples of NR/CB/leather and were assigned to the leather waste. A peak of Cr was found and related to the basic CrOHSO_4 used in the tanning process. The chromium waste was expected to be in the vulcanized NR

chains, but as observed in the leaching and solubilization tests shown in the Table IV, the quantities of chromium were much lower than the maximum value permitted.

Electrical Characterization

The impedance spectroscopy is a noninvasive technique for the investigation of complex processes from the electric and dielectric points of view being possible to investigate phenomena at zero field frequency and at a very high frequency. Figure 5 shows the experimental (points) and theoretical adjustment (lines) impedance diagrams at room temperature for the NR/CB, NR/CB/leather-60phr, and NR/CB/leather-80 phr composites with the corresponding EEC, whereas Table V lists the electrical values (R_1 , R_2 , C_1 , f_{01} , R_3 , C_2 , and f_{02}) obtained from theoretical adjustment with EEC. The theoretical adjustments of the impedance diagrams were a conventional approach to derive the electrical parameters of the sample. According to Figure 5(a), all of the diagrams exhibited some degree of decentralization, their shapes indicated that the electrical response was composed of at least two semicircles or relaxation phenomena, and each of them had a specific relaxation frequency, which created a semicircle. The best theoretical adjustment was obtained with a resistance (R_1) and two equivalent parallel RC circuits in series (R_2C_1 and R_3C_2), as shown in the inset of Figure 5(a). A good agreement between the experimental points and the theoretical curve was obtained with this circuit, and the list of values of resistance and C of composites is shown in Table V. For all of the composites, two relaxation phenomena were identified at $f_0 \approx 10^5$ and $\tau_0 \approx 6 \times 10^{-5}$ s, and both were associated with dipole orientation and ionic conduction because of the superficial charge on the CB and ions, lateral chains, and short molecules from the polymeric matrix and leather waste. The dispersion phenomena observed at low and high frequencies could be attributed to diverse effects, for example, to the electrode and I effects and interfacial polarization. The utilization of the sanitizing agents (B and D) did not change the shape of the curves significantly but, as required, decreased R of the samples and provided more free charge carriers for conduction.

The real part of the impedance $\{\text{Re}(Z^*)\}$ represents the resistance of an electrical element, and it is an important parameter used to characterize electronic circuits and components and to reflect the internal electronic structure of the material. $\text{Re}(Z^*)$ obtained at 273 K and normalized by Λ for the NR/CB, NR/CB/leather-60 phr, and NR/CB/leather-80 phr composites is

Table IV. List of the Principal Infrared Spectral Frequencies Between 4000 and 700 cm^{-1} for the NR/CB, NR/CB/Leather-60 phr, and NR/CB/Leather-80 phr Composites

Component	Band (cm^{-1})	Attribution	Component	Band (cm^{-1})	Attribution
NR and CB	3363	ν_s (O-H) _{absorbed}	NR, CB, and leather	1635	ν (C=O)
NR	2951	ν (C-H) _{olefin}	NR and leather	1537	ν (C=C) and ν (-NH)
NR, CB, and leather	2916	ν_{as} (-CH ₃ -CH ₂)	NR	1454	δ_{as} (-CH ₃)
NR, CB, and leather	2847	ν_s (-CH ₃ -CH ₂)	NR	1397	δ_s (-CH ₃)
NR	2361	ν_s (C-O)	NR	1078	ρ (-CH ₃)
NR	2338	ν_s (C=O)	Leather	1032	ν_{as} (-CO)
Leather	1734	ν (C=O)	NR	822	γ (C-H) _{olefin}

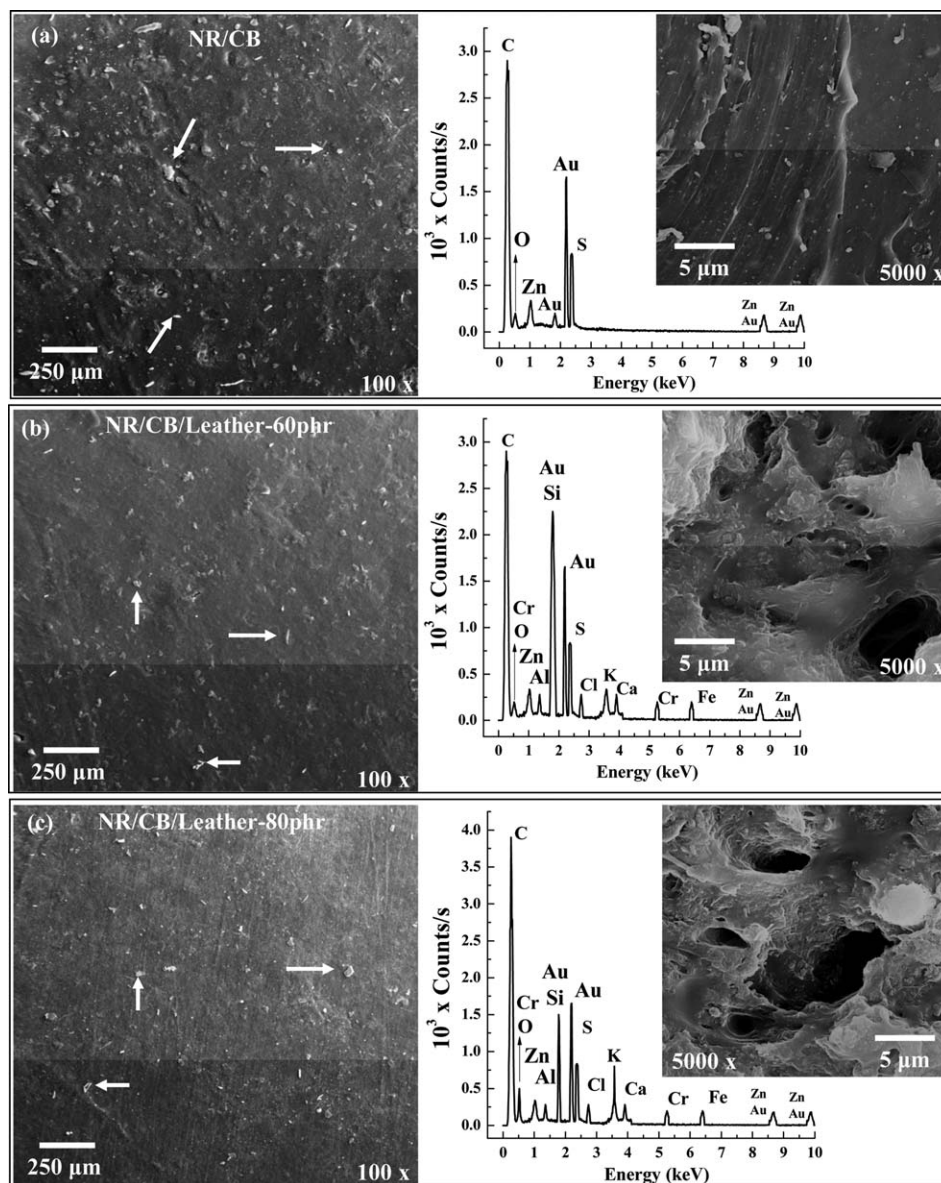


Figure 4. SEM images and EDX spectra at room temperature of the surfaces of the (a) NR/CB, (b) NR/CB/leather-60 phr, and (c) NR/CB/leather-80 phr composites at a magnification of 100 \times . The right-hand images are the SEM images of the fractured surface of the sample at a magnification of 5000 \times .

shown in Figure 6. As expected, the magnitude of this parameter was between 10^2 and $10^5 \Omega\text{m}$, which are typical values of the semiconductor materials used for electrical charge dissipation.²⁴ Three distinct ranges of evolution to $[\text{Re}(Z^*)]$ as a function of the frequency were identified. In the first range of frequency, between 10^{-1} and 10^5 Hz, a high value of the electrical resistivity (ρ) for the composites was found, but with the addition of leather waste and the exposure to sanitizing agents, ρ of the composites decreased as much as 300 times in comparison to NR/CB composites. When the frequency approached zero, these ρ values coincided with the values listed in Table VI. In the second range of frequency, between 10^5 and 10^6 Hz, there was a transition stage where the dipolar mechanism started to be sensitized by the field frequency. The exact frequency for the middle of this stage was the relaxation frequency, and it coin-

cided with the peak frequency in the imaginary part of the impedance $\{[\text{Im}(Z^*)]\}$ versus frequency (f) curve. In the last range, for frequencies more than 1 MHz, it was possible to observe a reduction of the resistivity and the predominance of only dipolar and electronic mechanisms. Similar assays were carried out by Odlyha et al.²⁵ in leather samples exposed to water for 24 h but with dielectric permittivity spectroscopy. The difference between the dry and exposed leather was approximately 2.5 times, as obtained here.

$[\text{Im}(Z^*)]$ represents the reactance of the system, and it is related to the electric and dielectric losses when an ac electrical field is applied. The frequency in which the loss is a maximum is named the relaxation frequency. Figure 7 shows $[\text{Im}(Z^*)]$ for the NR/CB, NR/CB/leather-60 phr, and NR/CB/leather-80 phr

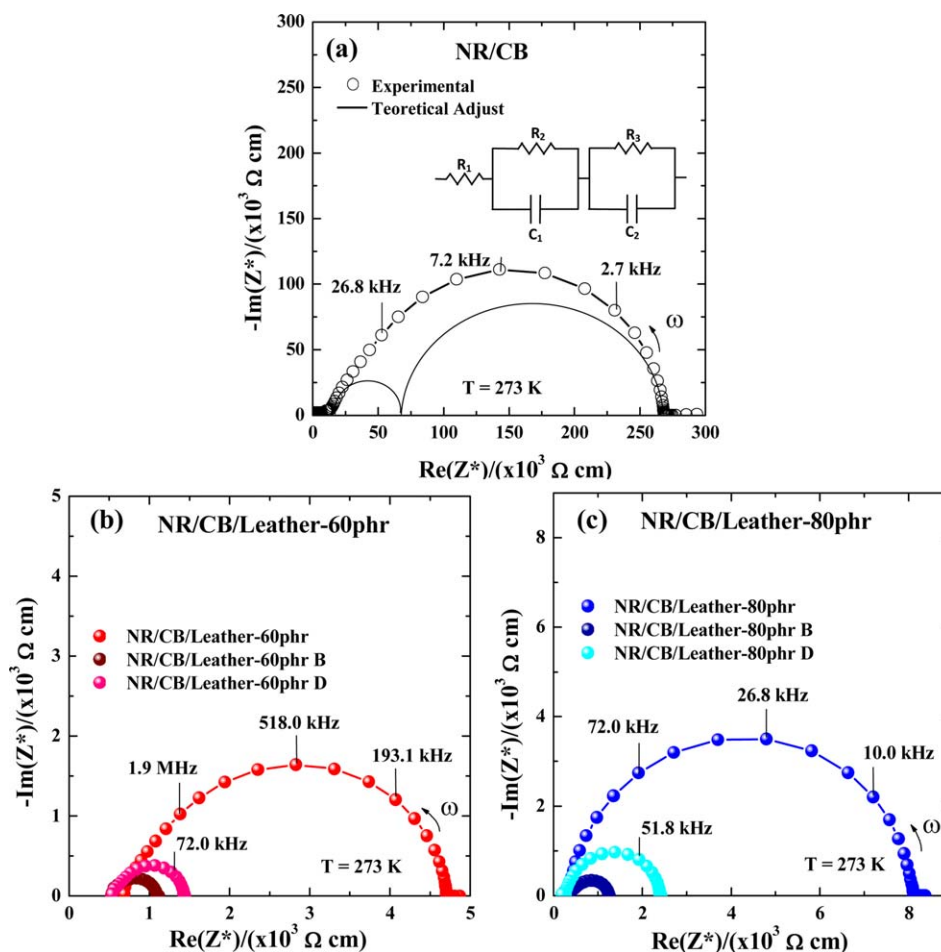


Figure 5. Experimental (points) and theoretical adjustment (lines) impedance diagrams for the (a) NR/CB, (b) NR/CB/leather-60 phr, and (c) NR/CB/leather-80 phr composites with the corresponding EECs obtained at a temperature (T) of 273 K. For some experimental points, the corresponding frequencies are given. Unfortunately, it was not possible to plot all of the experimental data on the same scale. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composites. The data were obtained at 273 K and normalized by Λ . As shown in Figure 7, apparently, all of the composites exhibited only one relaxation frequency. However, when the

high-frequency range was magnified, as shown in detail in Figure 7(b,c), and in accordance with the discussion of Figure 5, it was possible to identify the predominance of two electric loss

Table V. Values of the Electrical Components R_1 , R_2 , C_1 , f_{01} , R_3 , C_2 , and f_{02} Obtained from the Theoretical Adjustment with an EEC, as Shown in Figure 5 for the Composites

Composite	R_1 (Ω)	R_2 (Ω)	C_1 (F)	n_1	f_{01} (Hz)	R_3 (Ω)	C_2 (F)	n_2	f_{02} (Hz)
NR/CB	1.3×10^4	2.3×10^4	4.9×10^{-11}	1.0	1.4×10^5	2.3×10^5	9.6×10^{-11}	1.0	7.2×10^3
NR/CB/leather-60 phr	6.9×10^2	2.3×10^2	1.1×10^{-10}	0.9	6.2×10^6	3.8×10^3	8.1×10^{-11}	1.0	5.2×10^5
NR/CB/leather-60 phr B	0.53×10^2	7.0×10^2	1.6×10^{-11}	1.0	1.4×10^7	5.0×10^2	8.6×10^{-11}	1.0	3.7×10^6
NR/CB/leather-60 phr D	5.4×10^2	1.1×10^2	1.0×10^{-9}	1.0	1.4×10^6	9.3×10^2	1.2×10^{-9}	1.0	1.4×10^5
NR/CB/leather-80 phr	3.1×10^2	8.8×10^1	1.3×10^{-9}	0.9	1.4×10^6	7.7×10^3	6.5×10^{-10}	1.0	3.2×10^4
NR/CB/leather-80 phr B	3.4×10^2	1.2×10^2	1.3×10^{-9}	1.0	1.0×10^6	7.9×10^2	2.8×10^{-9}	1.0	7.2×10^4
NR/CB/leather-80 phr D	2.5×10^2	1.2×10^2	7.0×10^{-10}	1.0	1.9×10^6	2.0×10^3	8.0×10^{-10}	1.0	1.0×10^5

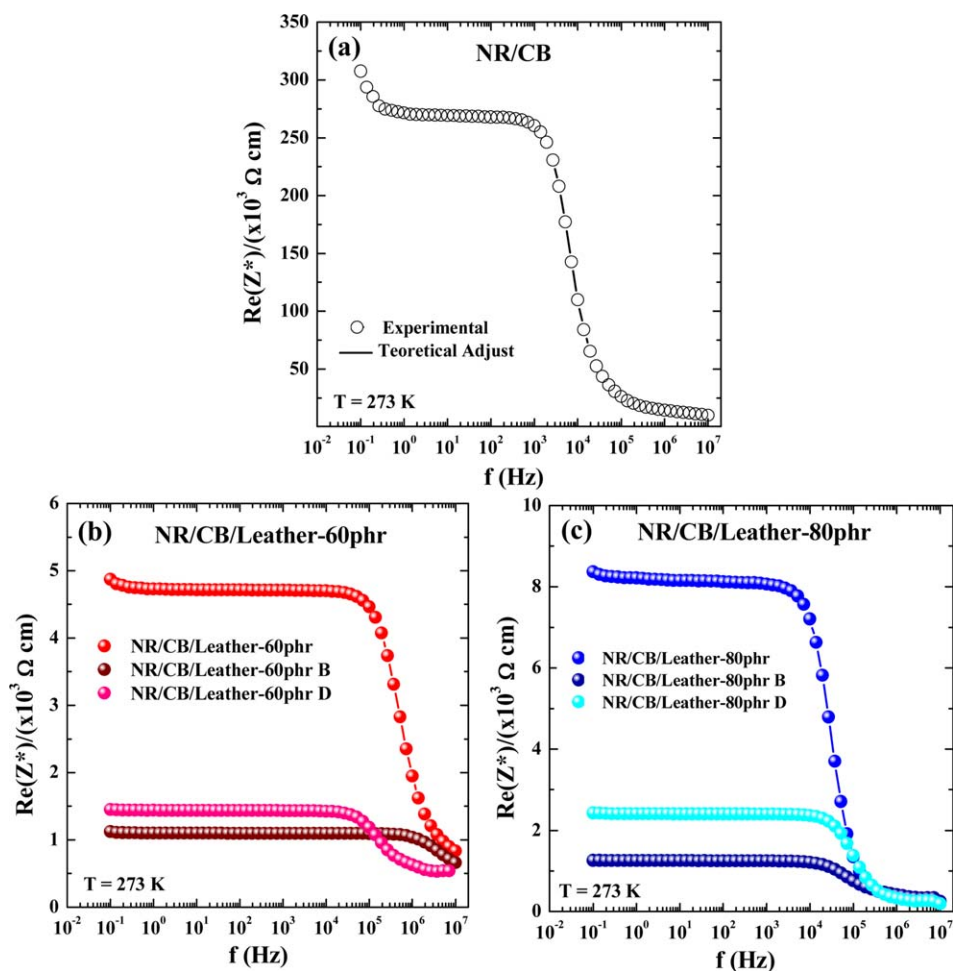


Figure 6. $\text{Re}(Z^*)$ at a temperature (T) of 273 K and normalized by Λ for the (a) NR/CB, (b) NR/CB/leather-60 phr, and (c) NR/CB/leather-80 phr composites. The points on the plot represent the experimental data, whereas the continuous lines represent the theoretical adjustment. Unfortunately, it was not possible to plot all of the experimental data on the same scale. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

processes. In this sort of system, it suggests that the friction between the main chains, superficial charges, movement of charge carriers, and small molecules was essentially responsible for the electric loss processes observed. On exposing the composites to the sanitizing agents, the intensity of loss processes decreased because of the reduction of R of the material. Odlyha et al.²⁵ reported similar results for the leather samples exposed to water for 24 h but with dielectric losses. In this case, the dielectric loss neared zero.

At zero field frequency, in the case of a dc situation, the electrical properties of the material were essentially represented by the Ohm resistance with its specific conductivity due to charge movements and a specific mechanism of conduction and charge transfers. The dc parameters are important references for anti-static flooring. Figure 8 shows the I versus V curves obtained at 273 K and normalized by Λ , whereas Table VI lists the values of Λ , ρ , and σ calculated by eq. (1) for the NR/CB and NR/CB/leather composites. According to Figure 8, all of the composites exhibited I versus V curves with linear evolution but with two different angular coefficients that indicated the presence of two distinct charge carriers or conduction mechanisms, as shown in

the discussion of Figure 5. In this kind of system, it suggests that the first conduction mechanism, in low voltage, was associated with superficial charge on the CB and the electrical trails generated by the CB. The second predominant mechanism of conduction, of greater voltage, was attributed to ions, lateral chains, and short molecules from the polymeric matrix and leather waste. The addition of leather waste and the exposure of

Table VI. List of Λ , ρ , and σ as Calculated by Eq. (1) for the NR/CB, NR/CB/Leather-60 phr, and NR/CB/Leather-80 phr Composites

Composite	Λ (cm)	ρ (Ωcm)	σ (S/cm)
NR/CB	1.436	1.75×10^5	5.70×10^{-6}
NR/CB/leather-60 phr	1.077	6.64×10^3	1.77×10^{-4}
NR/CB/leather-60 phr B	1.120	1.25×10^3	7.97×10^{-4}
NR/CB/leather-60 phr D	1.120	1.33×10^3	7.50×10^{-4}
NR/CB/leather-80 phr	0.824	1.53×10^3	6.52×10^{-4}
NR/CB/leather-80 phr B	0.782	9.23×10^2	1.08×10^{-3}
NR/CB/leather-80 phr D	0.814	5.20×10^3	1.92×10^{-4}

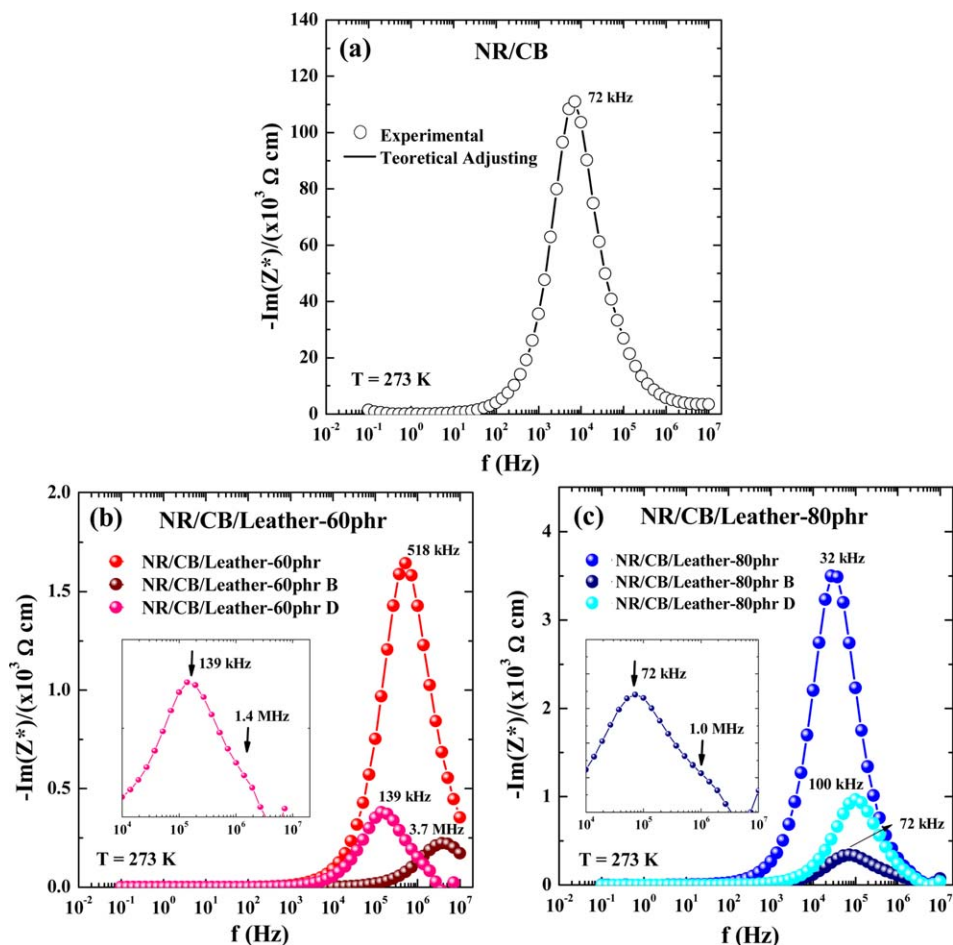


Figure 7. $[-\text{Im}(Z^*)]$ obtained at a temperature (T) of 273 K and normalized by Λ for the (a) NR/CB, (b) NR/CB/leather-60 phr, and (c) NR/CB/leather-80 phr composites. The points on the plot represent the experimental data, whereas the continuous lines represent the theoretical adjustment. In detail, as a model, the magnification of the high-frequency range shows the two relaxation processes. Unfortunately, it was not possible to plot all of the experimental data on the same scale. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

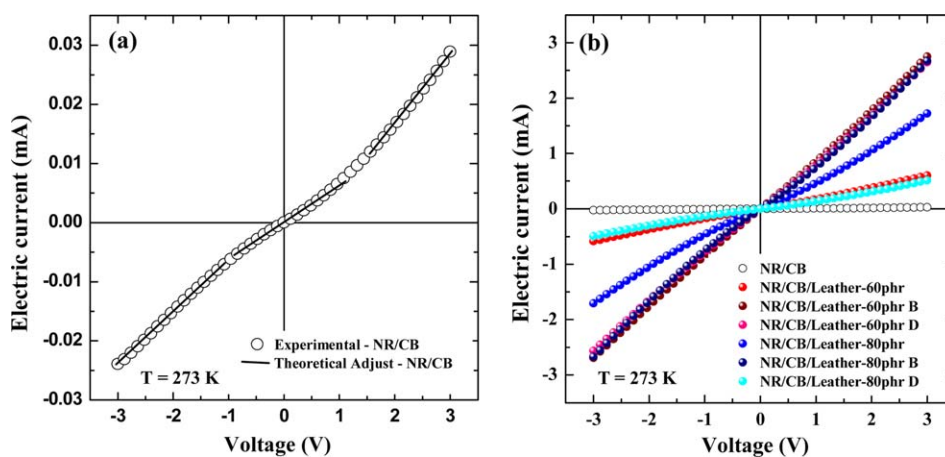


Figure 8. Electrical current versus voltage curves obtained at a temperature (T) of 273 K and normalized by Λ for the (a) NR/CB and (b) NR/CB/leather composites. The points on the plot represent the experimental data, whereas the continuous lines represent the theoretical adjustment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

them to the sanitizing agents increased their σ s two orders of magnitude from 5.70×10^{-6} for the NR/CB to 7.97×10^{-4} S/cm for NR/CB/leather-60 phr B and six orders of magnitude when compared to σ of NR, 1.0×10^{-12} S/cm.²⁶ Larger differences than these showed, depending on the geometric shape, surface properties and size distribution of the load, and they were only expected to concentrate near the percolation limit, which would have been close to 30% v/v for these kinds of materials. As a result, the NR/CB/leather composites started to exhibit characteristics of a semiconductor material; this makes these materials suitable to be used as an antistatic flooring.

CONCLUSIONS

Composites based on vulcanized NR, CB, and leather waste were prepared by thermal compression with 60 phr of CB and 60 or 80 phr of leather waste. This method was efficient for the preparation of such composites. According to Brazilian sanitary laws, these composites were exposed to B and D for 24 h with the aim of simulating a real situation of everyday use. As required, the structural and morphological characterizations of these composites did not show significant alterations in the material after exposure. From the ac and dc electrical characterizations, the addition of leather waste provided an increase of two orders of magnitude of σ . This parameter changed from 5.70×10^{-6} for the NR/CB to 7.97×10^{-4} S/cm for the NR/CB/leather-60 phr B and six orders of magnitude when compared to σ of NR, 1.0×10^{-12} . For both kinds of exposure to the sanitizing agents, σ of the composites improved up to 2.5 times principally because of the ions from the sanitizing agents that started to be suitable for electrical conduction in the composites. With these values of conductivity, the composites exhibited the potential to be used as an antistatic flooring. In this way, the development of these innovative composites based on NR, CB, and leather waste is an excellent option for allocation to leather waste because of the reduction of its environmental impact and as an opportunity to open up new economic possibilities for the leather industries. In addition, this new material has potential to be applied as an antistatic flooring.

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