

Chemical evaluation of composites natural rubber/carbon black/leather tannery projected to antistatic flooring

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ABSTRACT: In this study the composites which are commonly called NR/CB/Leather were developed in order to apply them as anti-static flooring and coating. They were developed using vulcanized natural rubber, carbon black to add an electric conduction property and industrial leather waste. The leather industrial waste was micronized and added to the rubber matrix in proportions of 60 and 80 phr using an opened mixing cylinder according to ASTM D 3182 standard. The composites were exposed to the sanitizing agents, (i) bleach and (ii) disinfectant, aiming to simulate a real cleaning context, and to meet the health standards of the Brazilian Ministry of health. Physical-chemical and microbiological evaluations were carried out to determine the structural and chemical stabilities of the composites. After this, low water absorption level (<1.5%), immobilization and low chromium oxide level (<1.5), pH within the neutrality rate and an excellent resistance to microbiological contamination were identified for the composites. Thus, from a physical-chemical perspective, the composites NR/CB/Leather displayed suitable properties and potential for application as antistatic flooring and coatings. Besides using leather industrial waste in their production, their manufacture can boost this industrial sector economically and, consequently, promote a reduction in environmental impact. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43618.

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INTRODUCTION

The continuous usage of leather has always escorted human evolution and has been influenced during the last century not only because of the speed of change such as the knowledge of diverse types of leather structures, research, and usage of new products and machines, but also because of the optimization of the current processes and operations. These changes were strongly determined by the increase in the use of leather, and by environmental requirements, especially in the last 30 years. Leather is a material which is produced by the physical (mechanic operations), chemical (processes), and structural transformation of the animal skin. The skin mainly consists of proteins, which are polymers resulting from the condensation of α -amino acid, in which a single molecule displays a great number of amino acids units that are joined together by peptide bonds. The tanning process, which is in other words, the transformation of skin into leather, is carried out in three main

stages: the *ribeira**, tanning, and finishing.¹ The *ribeira* is related to the initial phase when the fur and fat are removed; the tanning is when the reactions take place in order to transform the skin into a nonrotting material, namely leather, through the action of tanning reagents such as chromium basic sulfate or tannins; and finally, the finishing depending on the leather application, such as vehicle seats, shoes, clothes, and so on.^{2,3}

During leather processing, it is usual to generate large amounts of solid waste, especially organic waste. The potential for recycling may be improved by segregation, depending on the kind of waste.^{4,5} Leather waste is classified as Class I according to ABNT/NBR-10.004^{†,6} this solid acid possesses on average 3.5%

*Translator note (*Ribeira* process—wet part of tanning process, where the skin is prepared to receive the tanning agent).

†The Brazilian Regulatory Standards (NBR) are elaborated by Brazilian Association of Technical Standards (ABNT).

of trivalent chromium (Cr^{+3}), and depending on certain conditions such as, acid exposition, temperature, and chemical agents, it can lead to the production of hexavalent chromium (Cr^{+6}), that carries high potential for cutaneous contamination and also provokes cell alterations that cause different kinds of cancer.⁷

The alternative to commercializing this waste as by products is pertinent, as well as the cooperation among tanners to make the joint options of recycling and reuse feasible. The solid waste, produced by tanning, must be handled and stored in order to prevent odor problems, soil and water contamination, and atmospheric emissions.⁸ One of the possible options for reuse is the development of composites, in different mass proportions, through the mixing of natural rubber (NR) and carbon black (CB) together with vulcanization agents and leather waste.^{9,10}

Materials using NR and only CB have awakened great interest because of their technological application, since they possess excellent mechanical properties, easy processability, and electric conductivity.¹¹ With the acquisition of this new material it is possible to address an application for leather waste, generated in large amounts by tanneries, and therefore, minimize a serious economic and environmental problem. However, information about the chemical properties, sanitizing agents' influence on superficial properties, and information about the immobilization of chemical elements, such as chromium in composites that use leather waste, is scarce in scientific literature.

In this work, composites of vulcanized NR, CB and leather waste (NR/CB/Leather) were prepared for use as antistatic coating which results in an environmentally friendly use of leather waste products, including the immobilization of the chromium ions. Chemical and microbiological characterizations were carried out and the results were discussed, depending on the composite composition and the composite superficial exposition, using sanitizing agents.

MATERIALS AND METHODS

Preparation of the NR/CB-Leather Composites

Natural Rubber. Dry NR was used for the preparation of the composites (cis-1,4-polyisoprene) of the commercial variety CCB (*Crepe Claro Brasileiro*—CCB), financed by the *DLP Indústria e Comércio de Borracha e Artefatos (R)* in the city of Poloni/SP. This rubber is obtained in processing plants by the coagulation of latex from the *Hevea brasiliensis* species, clones RRIM 600.

Carbon Black. The CB used to produce the composites was N-330 of a purity greater than 99% financed by Columbia Petroleum Industry (R). This kind of CB has a density equal to 1.8 g/cm^3 , superficial area between 70 and $99 \text{ m}^2/\text{g}$ and 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.

Chemical Additives. The vulcanization activators were Zinc Oxide—ZnO (ZnO , 81.38 g/mol , A.P., Vetec) and Stearic Acid—St. Ac. ($(\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, 284.47 g/mol , A. P., Vetec). The antioxidant was the 2-Methyl-2-methylmercaptobenzimidazole

zinc salt - ZMB-2 ($\text{C}_{16}\text{H}_{14}\text{N}_4\text{S}_2\text{Zn}$, 391.83, A. P., Lanxess® Energizing Chemistry). Os aceleradores foram o 2,2 Dibenzothiazyl Disulfide—MBTS ($\text{C}_{14}\text{H}_8\text{N}_2\text{S}_4$, 332.49, A. P., Lanxess® Energizing Chemistry) and the Tetramethyltiuram Disulfide—TMTD $\{[(\text{CH}_3)_2\text{NCS}]_2\text{S}_2$, 240.43, A. P., Lanxess® Energizing Chemistry). The vulcanization agent was sulfur— S_8 (S_8 , 240.48 g/mol , A. P., Nuclear).

Leather Waste. The leather waste used for the preparation of the composites originated from the tanning process with basic chromo sulfate (CrOHSO_4). It is mainly made up of buffing, stripping, and shaving waste. The tanning process is responsible for providing mechanical stability and resistance to degradation of the material. The leather waste was financed by the Vitapelli Tannery^(R) in the city of Presidente Prudente/SP, Brazil. These materials were micronized and their pH was 16 maintained equal to 3.5 during processing.

Mix Procedure. 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. 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 react with each other to form zinc stearate $[2.(\text{C}_{17}\text{H}_{35}\text{COOH}) + \text{ZnO} \rightarrow (\text{C}_{17}\text{H}_{35}\text{COO}^-)_2\text{Zn}^{2+} + \text{H}_2\text{O}]$, sulfur (2.5 phr) and ZMB-2 (1 phr) and an accelerating system consisting of MBTS (1.2 phr) and Tetramethyltiuram Disulfide—TMTD (0.4 phr). 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 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 techniques of processing have been reported¹² and the components and their receptivity quantities for the composites are listed in Table I.

Chemical Attack with Sanitizing Agents: Bleach (B) and Disinfectant (D)

After the composites were produced, the chemical attack was carried out with the sanitizing agents bleach (sodium hypochlorite; active chlorine concentration from 2.0% to 2.5%) and disinfectant (ortho-benzyl-p-chlorophenol (0.25%) (ortho-phenylphenol (0.50%); water; active ingredients; soap; pine oil; solvent, stabilizer; and coloring) in accordance with the standards of the Health Surveillance Agency—Ministry of Health—Brazil. Afterwards, the chemical and microbiological analyses were carried out.¹³

Chemical Characterization of the NR/CB-Leather Composites

pH Tests. The pH analysis was carried out according to the NBR 11057/2006 standard.¹⁴

For this analysis, the samples were ground and mixed with distilled water (neutral pH) for 24 h using the slow stirring method. After the mixing process, the material was filtered and the pH measurements were applied in triplicate. The pH measurements were performed using a digital pH Meter of the brand

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

Samples	Concentration in phr ^a			Concentration in % w/w			Concentration in % v/v		
	NR	CB	Leather	NR	CB	Leather	NR	CB	Leather
NR/CB	100	60	–	62.5	37.5	–	75.0	25.0	–
NR/Leather	100	–	60	62.5	–	37.5	70.0	–	30.0
NR/CB/Leather-60 phr	100	60	60	45.4	27.3	27.3	56.8	18.9	24.3
NR/CB/Leather-80 phr	100	60	80	41.7	25	33.3	52.5	17.5	30.0

^aphr—Parts per hundred of rubber.

Nova Técnica calibrated with buffer solution of pH 4, 7, and 10. A certain quantity of the extract was separated in a hermetically sealed container and pH measurements were carried out at the following intervals of time 0, 10, 15, 30, 60, and 90 days in order to verify the pH evolution depending on the specific time.

Difference Figure Tests. In order to develop the assays of difference figure the same extract was used (composite + water) prepared for the pH tests diluted in 10 water parts. Afterwards, new pH measurements from dilution were carried out to obtain the difference figure using the relation: Difference Figure = pH_{Extract} – pH_{diluted}.

Chromium Oxide Determination. The determination of residual chromium oxide (Cr₂O₃) concentration in the composites was made using the (i) titrimetric method (Tit) and the (ii) Atomic absorption spectrometry (AAS) method.

Titrimetric method. This assay was carried out according to NBR-ISO 5398-1:2014 standard. Method “A”,¹⁵ while the material extract for the assay was obtained using standard procedures in accordance with NBR 11031/2013.¹⁶ In this method, the extract is exposed to a chemical attack with sulfur, perchloric, and nitric acids, with further titration of standardized sodium thiosulfate. The oxide chromium percentage determination was made using the following equation:

$$\text{Cr}_2\text{O}_3 = \left(\frac{100NV\text{Me}}{g} \right) \quad (1)$$

where Cr₂O₃ is the chromium oxide percentage concentration, *N* is the exact normality of the sodium thiosulfate solution, *V* is the volume spent of sodium thiosulfate in the titration, *g* is the mass of the composite sample and *Me* is milliequivalents gram of the chromium oxide (approximately 0.02533).

Atomic Absorption Spectrometry Method. In this assay, the oxide chromium concentration was determined using an AAS, flame modality, of the brand SpectrAA 50B Varian. At first a chromium standard solution was prepared for the construction of the calibration curve, in a concentration of: 1.0; 2.0; 4.0; 6.0; 8.0, 10.0, 15.0, and 20.0 ppm from the standard chromium stock solution 1000 ppm of the brand Carlo Erba. Nitric acid and water as a dissolution agent were used. The extract used in the assay was prepared from the pyrolysis of the composites to eliminate the organic matters. The composite ashes were dissolved using nitric acid, and after the concentration was adjusted in order to maintain the same level of acidity as the

standard acid used for calibration. The measurement parameters were: cathode lamp current equal to 7 mA, the carrier gases were acetylene and synthetic air, the wavelength equal 357.9 nm and a gap of 0.2 nm.

Water Absorption Tests. The water absorption determination was carried out according to the NBR-11130/2006 standard.¹⁷ A permeameter device of the brand MAQTEST was used to carry out the assays of absorbed and transmitted water. In this kind of assay, rectangular specimens are fixed on the base of the equipment and tensioned by water added during a previously determined time. The absorption percentage of water is estimated by the mass difference of the specimen before and after water exposition.

Leaching and Solubilization Assays. According to NBR 10005/2004,¹⁸ leaching assays are related to the determination of the transference capability of organic and inorganic substances present in solid waste, through the dissolution in the extractor solution number 2 (5.7 mL of glacial acetic acid and distilled water in a volumetric flask of 1 L). In turn, solubilization assays are performed according to NBR 10006/2004 standard in order to differentiate the classified waste, according to 10004/2004 as Class II A-noninert and Class II B-inert.¹⁹

Leaching. The leaching extract from solid waste was obtained based on the complementary standard NBR 10005/2004, in order to differentiate the waste as class I-hazardous and class II-nonhazardous. In this context, 5.0 g of composites NR/CB/Leather-60 phr and NR/CB/Leather-80 phr were ground and they resulted in particles of average diameters, approximately 9 mm, mixed with 96.5 mL di-ionized water and vigorously stirred for 5 min. The pH of the mixture was adjusted to 5 using hydrochloric acid 1 *N*, the extractor solution number 2 was added. The system was stirred for 20 hours and filtered. The leaching samples were submitted in order to determine the concentration of contaminants according to NBR 10004/2004 standard, via Atomic Absorption Spectrometer (ASS) Varian—SpectrAA—flame modality.

Solubilization. The solubilization assays were carried out according to NBR 6 10006/2004 to differentiate the waste classified at ABNT NBR 10004 as class II A-noninert and class II B-inert.⁶ In order to obtain the solubilized extract, 100 g of composites NR/CB/Leather-60 phr and NR/CB/Leather-80 phr were ground and kiln-dried at a temperature of 42 °C, determining the percentage of moisture. Portions of these composites

Table II. List of Values for the Equivalent Resistance and Capacitance, Main Relaxation Frequency, Electric Resistivity, and Conductivity of the Composites

Composites	R_{Eq} (Ω)	C_{Eq} (F)	f_0 (Hz)	ρ (Ω cm)	σ (S/cm)
- NR/CB	2.66×10^5	8.31×10^{-11}	7.2×10^3	1.75×10^5	5.70×10^{-6}
- NR/CB/Leather-60 phr	4.72×10^3	6.48×10^{-11}	5.2×10^5	6.64×10^3	1.77×10^{-4}
- NR/CB/Leather-60 phr B	1.25×10^3	3.44×10^{-11}	3.7×10^6	1.25×10^3	7.97×10^{-4}
- NR/CB/Leather-60 phr D	1.58×10^3	7.20×10^{-10}	1.4×10^5	1.33×10^3	7.50×10^{-4}
- NR/CB/Leather-80 phr	8.10×10^3	6.14×10^{-10}	3.2×10^4	1.53×10^3	6.52×10^{-4}
- NR/CB/Leather-80 phr B	1.25×10^3	1.77×10^{-9}	7.2×10^4	9.23×10^2	1.08×10^{-3}
- NR/CB/Leather-80 phr D	2.37×10^3	6.72×10^{-10}	1.0×10^5	5.20×10^3	1.92×10^{-4}

were mixed to di-ionized water and left to stand for 7 days at a temperature of 25 °C. The solution was filtered and the solubilized extract was analyzed according to NBR 10004/2004 standard, using an Atomic Absorption Spectrometer (AAS) Varian—SpectrAA—flame modality.

Microbiological Tests. The microbiological analysis was carried out to assess the material's behavior before microorganism contamination, as well as the efficiency after treatment with sanitizing products, because the material is to be used for domestic or commercial flooring and coating. As contamination materials, fungi from the *zygomycetes* group was selected as well as bacteria from the *enterobacteriaceae* group, which are microorganisms that are usually present in a domestic environment. The methodology used to carry out the microbiological analysis was the one described in chapter 48 of book “*Bacteriologia e Imunologia*”, with respect to its applications in the areas of medicine and hygiene, by Otto Bier, 20th Edition, from University of São Paulo published, 1980.²⁰ This methodology determines the formulation of culture media that is used to observe microorganism of several classifications: Bacteria, fungi, protozoan, and seaweeds, and the interpretation of the microbiological results for the necessary care and sterilization. The slides were prepared, and microbiological structures were analyzed using a microscopy of the Nova Optical System brand, model 107, in amplification of 40 \times , 100 \times , and 400 \times , that corresponds to a visual field of 480, 200, and 48 μ m, respectively.

Electric, Mechanical, and Structural Characterizations of the NR/CB-Leather^{9,10}

Having established the objective of the use of NR/CB-Leather composites as a raw material for antistatic flooring, the determination and modulation possibility of the material's electric, mechanical, and structural properties are pivotal to the development process of the technology. The electric properties of these composites were studied by Ruiz *et al.*⁹ and Table II enumerates the identified values for the equivalent resistance and capacitance, frequency of main relaxation, resistivity and conductivity of the composites. The main information about the mechanical and structural properties of the composites were presented by Ruiz *et al.*^{9,10} as Supplementary Information. In general lines, electric, mechanical and structural characteristics are suitable for antistatic flooring. The schematic representation of the gen-

eral preparation process and chemical characterization for the composites is shown in Figure 1 (Table II).

RESULTS AND DISCUSSION

Potential of Hydrogen (pH) and Difference Figure

For an adequate chemical evaluation, pH assays are extremely useful for verifying the acid levels in which the materials are found. The chemical stability of a material is directly related to pH values, once chemical reactions depend on specific values for its occurrence. While the pH values of the untreated materials (black points), exposed to bleach (red points), and disinfectants (blue points) are shown in Figure 2(a), Figure 2(b) shows the pH evolution according to time, 0, 10, 15, 30, 60, and 90 days, for the NR/CB/Leather-80 phr samples. However, even after exposing the material for 90 days, the pH values remained within the neutrality rate. For the samples submitted to

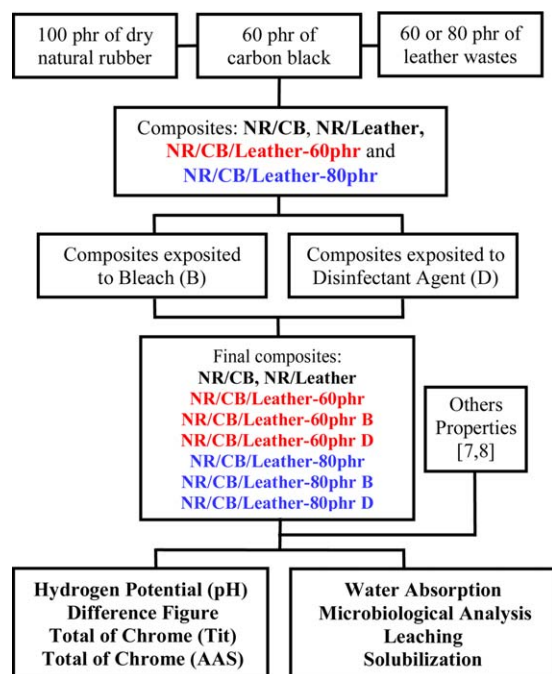


Figure 1. Flow-chart for the fabrication of the NR/CB, NR/Leather, NR/CB/Leather-60 phr and NR/CB/Leather-80 phr composites, as well as, the chemical characterization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

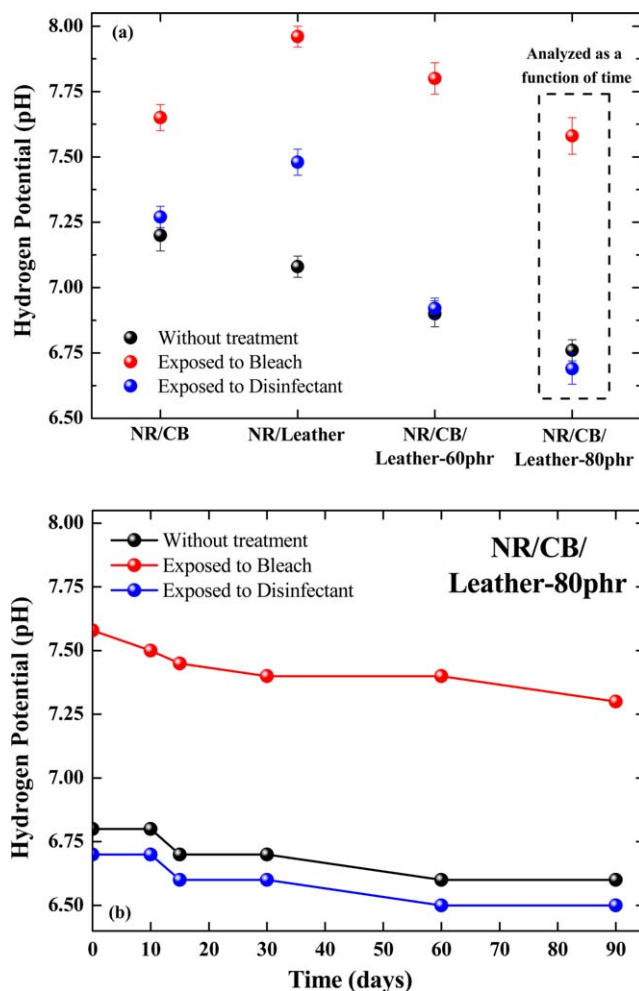


Figure 2. Potential hydrogen (pH) of the NR/CB, NR/Leather, NR/CB/Leather-60 phr, and NR/CB/Leather-80 phr composites (a). Evolution of pH as a function of time (days) for the NR/CB/Leather-80 phr composite (b). All the assays were realized without treatment (black lines), exposed to bleach (red lines) and to disinfectant (blue lines). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

treatment with bleach of a chemical composition: sodium hypochlorite and active chlorine concentration (2.0–2.5% m/m) the pH values were higher, as can be observed in Figure 2. These results were probably consequences of the sodium hypochlorite's chemical composition that presents pH variation between 12 and 13.²¹ Considering that the composites remained exposed in bleach for 24 h, there is the possibility of a sodium hypochlorite residual that resulted in superior pH values. The results obtained during the 90 day period showed a pH decrease in all the samples. This result was expected, since the contact with carbon dioxide in air acidifies water, resulting in a pH reduction. This reduction was minimal since the sample was kept in a sealed container. The carbon dioxide diluted in water generates carbonic acid through the following chemical balance:



Therefore, even though the carbon dioxide does not cause a high level of acidity in water, it is an important component because of its presence, whether through its dissolution in

water, originating from the atmosphere, or by partial pressure difference (Henry law).²² For the samples exposed to the sanitizing agent disinfectant, the chemical disinfectant composition (ortho-benzyl-p-chlorophenol 0.25%, ortho-phenylphenol 0.50%; water; active ingredients formaldehyde; soap, pine oil solvent; stabilizer; sequestrant, and coloring) does not influence the pH variation of the materials, and the results were very similar to the samples which had not been treated with sanitizing agents. Considering that the disinfectant's pH rate of the aforementioned chemical composition is between 6.5 and 7.4, i.e. within the neutrality rate, it was concluded that the composites were not influenced by the chemical composites found in the disinfectant. The same result could be observed in the assay during a period of 90 days. From a commercial point of view, this stability demonstrated by the pH results, guarantees the material application as flooring and coating.

The difference figure assays are widely used to analyze the pH variations when materials are submitted to an excessive amount of water. Figure 3 shows the difference figure parameter's values for the composites NR/CB, NR/Leather, NR/CB/Leather-60 phr, and NR/CB/Leather-80 phr without treatment, exposed to bleach and disinfectant. For the assays performed with and without superficial treatment (bleach and disinfectant) the difference figure evolutions were clear, demonstrating that the pH variation of the samples is within an acceptable tolerance range. Taking into consideration that the ideal results for this characterization is a difference figure lower than 0.7, all the composites presented parameters below 0.7,²³ the stability of the material is demonstrated, as well as its resistance to excessive water exposition. The samples treated with bleach showed smaller difference figure alterations, indicating superior chemical stability compared with the others.

Chromium Oxide Concentration (Cr_2O_3)

Estimating the chromium oxide concentration in composites that use leather waste such wet-blue is pivotal to test its viability for commercial use, since the chromium oxide, in favorable

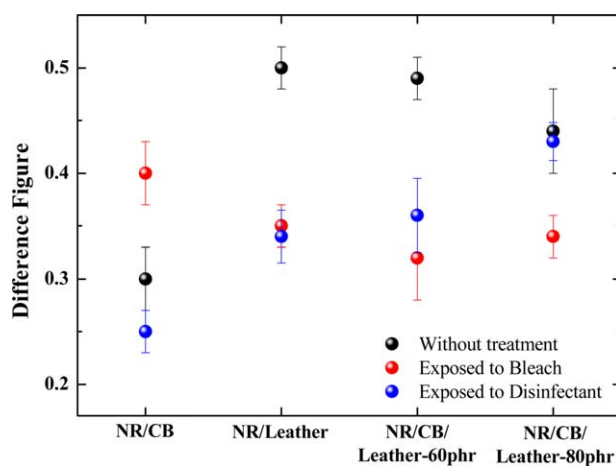


Figure 3. Difference figure of the NR/CB, NR/Leather, NR/CB/Leather-60 phr, and NR/CB/Leather-80 phr composites without treatment (black lines), samples exposed to bleach (red lines) and to disinfectant (blue lines). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

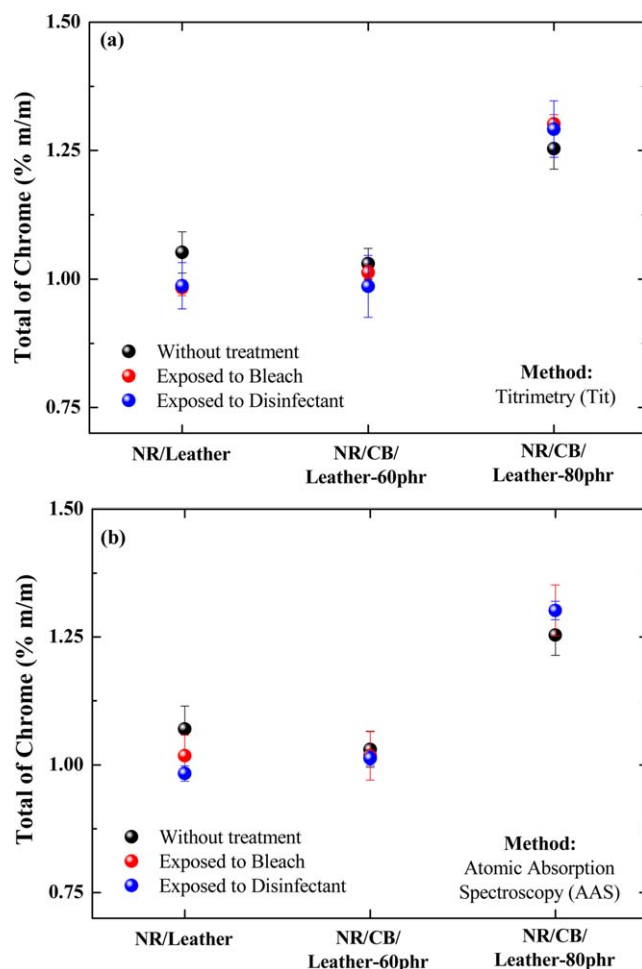


Figure 4. Evolution of the Chromium Oxide percentage concentration estimated by titrimetric method (Tit) (a) and Atomic Absorption Spectrophotometry (AAS) (b) for the composites NR/Leather, NR/CB/Leather-60 phr and NR/CB/Leather-80 phr. All the assays were carried out for samples without treatment (black points), exposed to bleach (red points) and to disinfectant (blue points). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

environmental conditions, can undergo a chemical alteration and also increase its toxicity levels, resulting in damage to the environment and the consumer. Figure 4 shows the evolution of the chromium oxide percentage concentration estimated by titrimetric method (Tit) (a) and Atomic Absorption Spectrophotometry (AAS) (b) for the composites NR/Leather, NR/CB/Leather-60 phr and NR/CB/Leather-80 phr without treatment as well as after treatment with bleach and disinfectant. As expected, the chromium oxide concentrations obtained in both methods (Tit) and (AAS), were similar, within the margin of error of the equipment, and the composite NR/CB/Leather-80 phr was the one that showed a higher concentration of chromium oxide, because of the bigger leather waste fraction in its composition. Once the leather wastes fibers were dispersed among the vulcanized NR chains, the chromium oxide concentration for the samples exposed to different kinds of sanitizing agents did not present significant differences. It is worth emphasizing that the chromium oxide percentage presents cor-

relation with the chromium oxide concentration in the leather. The mass percentage of leather in the composites is on average 25%, with a minimum of 3, 5–4% chromium oxide. As is already known, chromium oxide displays, predominantly, trivalent ions and hexavalent ions in minority.²⁴ In the case of wet blue leather waste trivalent chromium concentrations equal to 3.14% (m/m) were identified, using the titrimetric technique (Tit), and 3.17% (m/m) using the spectrophotometric technique (ASS). As for the hexavalent chromium ions, the quantitative is 400 times smaller than the trivalent ions range. In percentage terms, the hexavalent ions represent only 0.01%.²⁵ Using the ASS technique, the percentage in mass of total chromium was determined, whereas with the Tit technique, the percentage according to the chromium oxide (chromium trivalent) was determined. Thus, a small concentration difference was identified, on average 0.005% m/m. Such a difference could be related to the chromium's specificity that, because of oxidation processes, would form the chromium VI. However, this percentage value is near the limit of detection of the equipment.

Water Absorption Analysis

As the composites are to be used in antistatic flooring, absorption water assays are relevant because excessive water absorption results in an alteration of the mechanical properties, drying time and the material's capability of electric conduction. The percentage of water absorption for the composites NR/CB, NR/Leather, NR/CB/Leather-60 phr and NR/CB/Leather-80 phr, with and without treatment with bleach and disinfectant, are shown in Figure 5. Once the leather wastes fibers are dispersed among the vulcanized NR and the vulcanized NR displays a high level of impermeability, the percentage of water absorption for the samples, with and without exposition to the different kinds of sanitizing agents, are not significant and are inferior to 0.12%. Such results prove that the composites are suitable for use in humid environments, and even in extremely humid

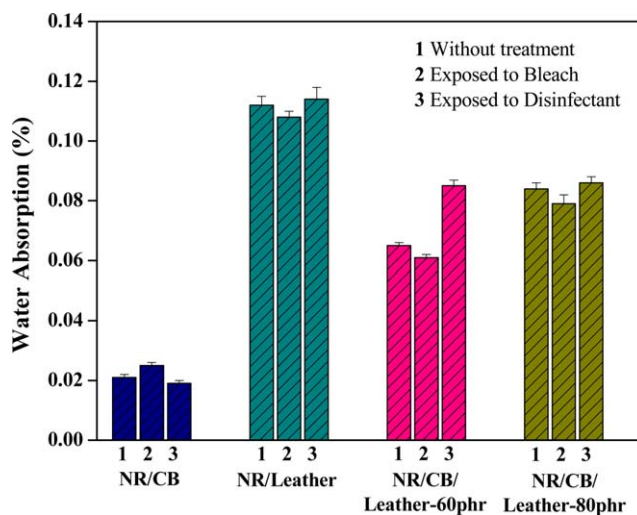


Figure 5. Evolution of the percentage of water absorption for the composites NR/CB, NR/Leather, NR/CB/Leather-60 phr and NR/CB/Leather-80 phr composites without treatment (bars 1), samples exposed to bleach (bars 2) and to disinfectant (bars 3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. List of Concentration and Maximum Value Permitted (MVP) for the Identified Elements in the Leaching Tests Realized in the NR/CB/Leather-60 phr and NR/CB/Leather-80 phr Composites

Tests	Composites	NR/CB/Leather-60 phr		NR/CB/Leather-80 phr	
		Concentration (mg L ⁻¹)	MVP (mg L ⁻¹)	Concentration (mg L ⁻¹)	MVP ^a (mg L ⁻¹)
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

^aMVP = Maximum Value Permitted.

nd = Not detected.

conditions. In the work developed by Pigatto *et al.* (2009),²⁶ polypropylene composites and blends reinforced with sisal fibers were prepared, and the results indicated that increased water absorption depended on an increase in the concentration of sisal fibers. As in the case of leather waste, the sisal fibers also display a hygroscopic character.

Leaching and Solubilization

Leaching and solubilization assays are commonly used to determine or evaluate the chemical stability of the waste when exposed to an aqueous solution, and they also allow the immobilization level of contaminants to be verified, besides the waste level of activity (inert or noninert). Tables III and IV list the identified elements in leaching and solubilization assays for the composites NR/CB/Leather-60 phr and NR/CB/Leather-80 phr.

As expected, once the leather waste fibers are dispersed among the vulcanized NR chains and the vulcanized NR exhibits a high level of impermeability, the composites present concentrations below the maximum value allowed for each chemical species. The residual values identified in the samples are especially associated to superficial waste of the composite preparation process, such as excessive vulcanizing agents, that naturally display outcrop processes. Especially for chromium metal found in leather, the identified concentration was below the limit value allowed, which characterizes an important result for the disposal of the material after use. Thus, bearing in mind the elements and chemical composite release, such materials are suitable when exposed to weathering conditions and/or washing processes without significant release of chemical elements in the environment after their operational life. Therefore, they could

Table IV. List of Concentration and Maximum Value Permitted (MVP) for the Identified Elements in the Solubilization Tests Realized in the NR/CB/Leather-60 phr and NR/CB/Leather-80 phr Composites

Tests	Composites	NR/CB/Leather-60 phr		NR/CB/Leather-80 phr	
		Concentration (mg L ⁻¹)	MVP (mg L ⁻¹)	Concentration (mg L ⁻¹)	MVP ^a (mg L ⁻¹)
Solubilization	Aluminum	0.10 ± 0.01	0.20	0.15 ± 0.01	0.20
	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

^aMVP = Maximum Value Permitted.

nd = Not detected.

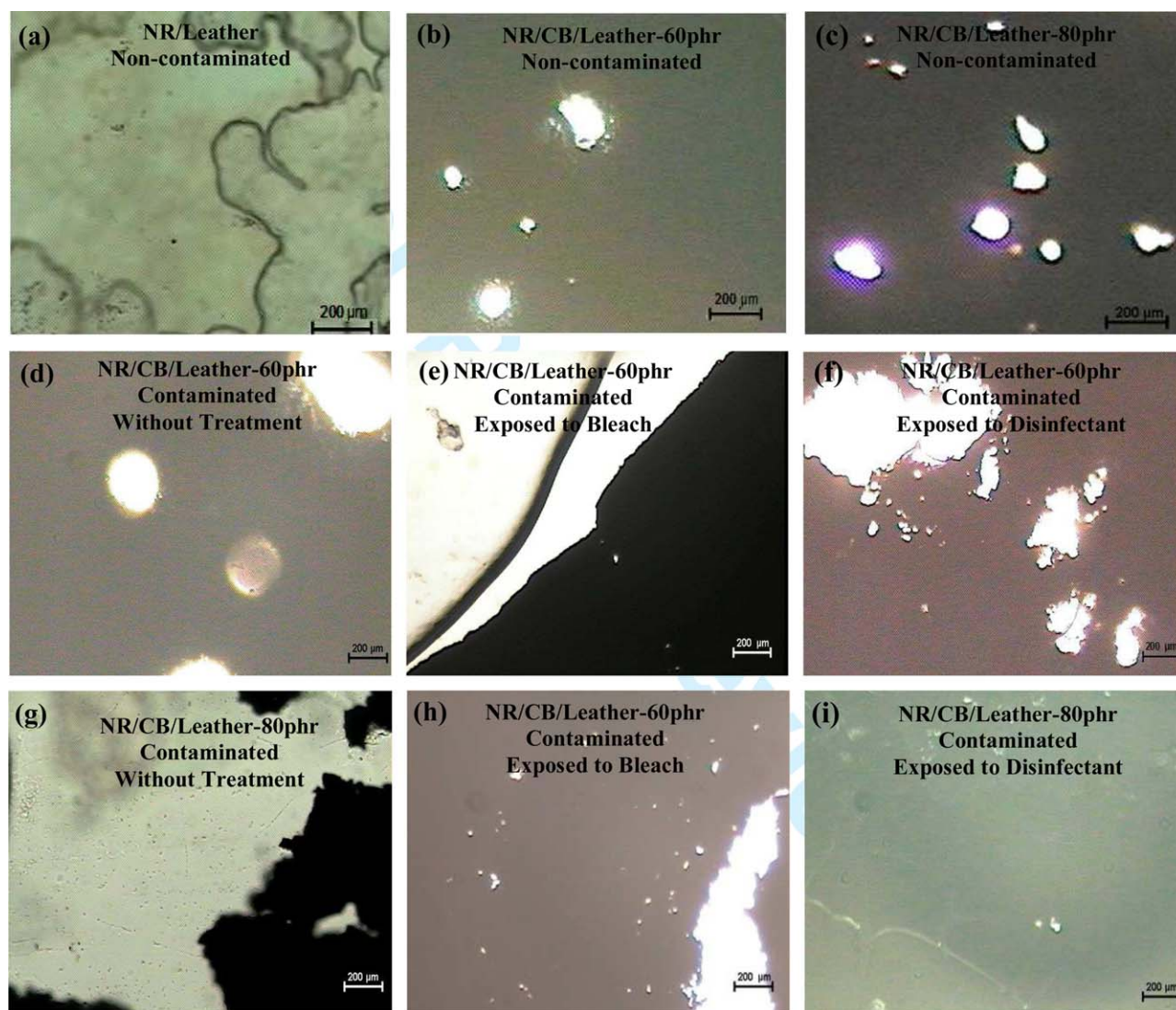


Figure 6. Images of microbiological tests: (a) NR/Leather, (b) NR/CB/Leather-60 phr and (c) NR/CB/Leather-80 phr without treatment; (d) NR/CB/Leather-60 phr without treatment, (e) NR/CB/Leather-60 phr exposed to bleach and (f) NR/CB/Leather-60 phr exposed to disinfectant; and (g) NR/CB/Leather-80 phr without treatment, (h) NR/CB/Leather-80 phr exposed to bleach, and (i) NR/CB/Leather-80 phr exposed to disinfectant. The samples (a), (b), and (c) were not contaminated and the other samples were contaminated by fungi and bacteria. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be classified as nonhazardous materials. The solubilization assays did not indicate a significant amount of the chemical species in accordance with the leaching assays. By way of comparison, solubilization assays in leather waste were also carried out. In the case of wet blue leather, which was obtained fresh from the production line, the results were in disagreement with current legislation. This kind of leather is normally disposed of in the environment. The parameters that are not followed are: aluminum; total chromium, iron, manganese, the total chromium concentration being equal to 0.064 mg L^{-1} with a maximum limit of 0.05 mg L^{-1} .²⁷ Therefore, it attests that the preparation process of the composites NR/CB/Leather-60 phr e NR/CB/Leather-80 phr, besides adding an economic and technological value to waste that involves high disposal costs in legal industrial landfills, still reduces potential impact on the environment.²⁸

Microbiological Analysis

The microorganisms use the carbon as an energy source for their metabolism and the composite components possess carbon in their structures. In this way, organic carbon sources, such as, leather can be attacked by microorganisms.²⁹ The leather stability, provided by the chromium metal bonds, makes a microorganism attack less likely.²⁶ However, it is necessary to consider the processes and operations previous to the chemical reaction with the chromium. One of the operations that is worth mentioning is called defleshing (removal of the hypoderm). When this process does not occur completely, the skin may contain an excess of natural oil, carbon source, which contributes to the development of microorganisms, such as fungi and bacteria. Figure 6 shows images of microbiological tests: (a) NR/Leather, (b) NR/CB/Leather-60 phr and (c) NR/CB/Leather-80 phr without treatment; (d) NR/CB/Leather-60 phr without treatment,

(e) NR/CB/Leather-60 phr exposed to bleach and (f) NR/CB/Leather-60 phr exposed to disinfectant; and (g) NR/CB/Leather-80 phr without treatment, (h) NR/CB/Leather-80 phr exposed to bleach, and (i) NR/CB/Leather-80 phr exposed to disinfectant. The samples (a), (b), and (c) were not contaminated and the other samples were contaminated by fungi and bacteria. The composites NR/CB/Leather-60 phr and NR/CB/Leather-80 phr present in the visual field 200 μm a structure maintenance, including the material integrity, which hinders the passage of light, that are only visualized where perforations were made during the cutting in the microtome. It is possible to verify that the structures do not display degradation signals because of the action of microorganisms. Thus, it is attested that, for all the samples, the microbiological structures remain unchanged, allowing it to be concluded that the material quality was conserved, not only in relation to the chemical agents used, but also to the microbiological agents.

CONCLUSIONS

The composites NR/CB/Leather developed for application as flooring and coating displayed chemical stability which was proved by the pH analysis. Composites with a pH between 6.6 and 8.0 were obtained, considered within the neutrality rate, even when exposed to sanitizing agents. The difference figure displayed pH variations below the limit established by the NBR 11057 standard, which proves stability even when floors are cleaned. Concerning the quantity of chromium in trivalent form, the average percentage 1% was in accordance with the amount of leather waste applied in the formulation. The range of water absorption of the composites indicated extreme impermeability, which is an ideal property for floor and coatings. The leaching analysis proved that the material does not contaminate the environment, since all the metals analyzed leached below the maximum limit established by the NBR 10004 standard. By means of the leaching assay, it was possible to classify the composites as class II, in other words, nonhazardous waste. In the solubilization assays, the metals did not solubilize over the allowed limit. In this way, the waste of the composites NR/CB/Leather was classified as Class II – A, in other words, nonhazardous and noninert, the classification as noninert refers to the combustibility of the material. As for the microbiological analysis, the material was very resistant to contamination by fungi and bacteria. This result guarantees the application, for example as a countertop coating, where the contact with the user is greater. In this way, the use of leather waste in the production of the composite NR/CB/Leather will contribute to the reduction of environmental liabilities as well as adding economic value to a waste product that currently generates expense for its disposal.

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