

Article

# Selection of Tanned-Leather Waste in Recovering Novel Raw Material for Manufacturing Rubber Artifacts: Towards a Zero-Waste Condition

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**Abstract:** Zero-waste is an ambitious goal to encourage sustainable production, consumption optimum recycling and resource recovery. The recycling and resource recovery of chrome-tanned leather waste is a difficult proposition because of the three-dimensional chemical network of collagen, which renders leather waste incompatible to polymer matrices. Many attempts have been undertaken to reuse leather waste, most of them require technological processes and challenging chemical pretreatments, which make the reuse an economically disadvantageous industrial operation. The paper aims to show how a very fine separation of leather solid waste leads to raw materials suitable for mixtures with natural rubber, without any chemical pretreatment. In other words, the paper intends to be a stimulus to manage leather solid waste carefully to start a cleaner and more profitable production. In particular, various industrial compounds containing different concentrations of post-tanning dyeing, or chrome shaving or oil-tanning and natural rubber were vulcanized through a standard preparation. Some compounds were also reinforced with carbon black and the vulcanization kinetics were monitored through rheometer. Experimental results indicate that there exists an optimal concentration of waste such that post-tanning dyeing post-tanning and chrome shaving are suitable for manufacture floor mats, soles and heels while oil-tanning waste can be used for making hose or conveyor belts. The mechanical performances of the articles prepared by direct mixing with leather waste are the same as those of commercially distributed rubber products.

**Keywords:** leather waste; recycling; vulcanization; manufacturing

## 1. Introduction

The transformation of animal skins and hides into the manufacture of commercial products requires a series of chemical and mechanical processes. During the transformation, a large amount of solid organic waste characterized by skin trimmings, fleshing waste, chrome shaving and buffing waste is generated [1–3]. Leather waste is mainly composed of collagen fibers cross-linked in a three-dimensional structure [4,5]; hence, its landfilling involves long decomposition times. In addition, the incineration of this waste requires a large amount of energy with the risk, for chromium-tanned waste, of releasing Cr(VI), making its disposal or reuse hard [6]. The main difficulty encountered in the disposal or use of tanned waste is the presence of heavy metals. Several studies to immobilize [7] or strengthen chromium fixation [8] on skins, have been evaluated and alternative chrome-free tanning systems have been made [9,10]. It is, therefore, not surprising that numerous studies have focused on reducing the environmental impact and making the process sustainable [11]. The strategies adopted concern both the depollution of effluent streams [12] and the chemical treatment of solid waste.

Generally very aggressive methods are used [1] such as co-digestion [13], pyrolysis[6,14], incineration to inert the chromium [15], steam gasification [16], biogas production [17] or biodiesel [18] chromium acid extraction to formulate fertilizers [19]. Such methods have a major economic impact so that only exceptional proposed strategies can be made operational. Anyhow, most industrial applications seek to use only non-tanned solid waste to reduce the risk of chromium release. Nevertheless, due to the greater awareness of environmental issues, the management of solid tanned waste over the past few years has taken on a primary role for the tanning industries. Interest has recently renewed for solid tanned waste in the field of polymers [20–23].

The poor compatibility with polymer matrices (especially thermoplastics) due to their hydrophilic behavior still represents a major limitation for a wider industrial exploitation of natural fibers such as, for example, tanned leather. Several efforts to enhance the interfacial adhesion of natural tanned leather fibers have been proposed [22], but their industrial implementations are often complicated by the large amounts of chemicals involved or the multiple processing steps required. The aim of the work is to stress that a strategy can be carried out to use, without any pretreatment, the most suitable tanned waste for the production of specific rubber products, the choice is made according to zero-waste condition [24], which may be achieved by applying the requirements of maximum separation and minimal wrecking [25]. A very careful separation of leather waste, along the entire production chain, leads to the identification of homogeneous classes of by-products, which behave as raw materials. These can be used for manufacturing novel products without wrecking the intrinsic structure of leather waste, with a net economic saving [25]. Furthermore, the life cycle material is lengthened and the environmental impact significantly reduced. Mechanical properties of final products were tested by measurement of strength, bending, hardness and impact resistance. Mechanical properties were also used to determine the range of usefulness of the material. Accordingly, car mats, soles and heels for footwear, non-slip grip for chairs and laminate floor coverings were manufactured.

## 2. Materials And Methods

### 2.1. Materials

Natural rubber (NR) and all solvents used in this research were technical grade reagents (RE) purchased from Carlo Erba Reagents. Reinforcing of compounds was performed by carbon black (mesoporous graphite with specific surface greater than  $500 \text{ m}^2\text{g}^{-1}$ ), purchased from Sigma Aldrich.

Leather waste to manufacture compounds and finished products, were taken from a plant for tanning processes to which various Solofra tanneries contribute (Avellino, Italy). The waste was chosen to cover three different stages of the tanneries' processing. In particular post-tanning dyeing (PTD) (cattle hides), chrome shaving (CS) (goat skins) and oil-tanning (OT, sheepskin). Furthermore, PTD and CS were stabilized by dried at  $60 \text{ }^\circ\text{C}$  until 10–14% of relative humidity was reached. For OT samples, a stabilization procedure was not necessary because the stability was ensured by its humidity. Chemical analyzes on raw materials were discussed in a previous paper [25].

### 2.2. Preparation of Rubber Compounds

To produce rubber articles having the proper elastomeric physical properties, the polymer chains must be very flexible and chemically cross-linked. A base compound (BC) was made through a standard rubber preparation process using NR as a matrix, the compositions of which are detailed in Table 1. In this table, we show the different functions and well-known ingredients used for industrial compounds. Briefly, a sulfur-based cross-linking vulcanization rate system is used. Since the vulcanization with sulfur alone is slow, chemical accelerators and activators are necessary. In addition, zinc oxide and stearic acid are included in the system. A large amount of calcium carbonate is added to increase the product's volume and reduce the cost of rubber articles. The BC compound was used as a reference material to compare the physical properties of all formulations investigated. Rubber compounds were prepared mixing BC compounds with appropriate quantities of PTD, CS and OT,

as detailed in Table 1. Leather waste PTD and CS were size-reduced with knife-mill (Wiley-model) and passed through a 3-mm-mesh sieve. Milled leather waste is reported in Table 1 with the prefix M, cutouts of OT appeared in grains smaller than 1-mm, hence they were used without further milling.

The composition of all formulations, expressed as parts per hundred of rubber (phr), are summarized in Table 1. The specimens for vulcanization were prepared by means of a pneumo-hydraulic press (NOSELAB ATS s.r.l.). The mixture was kept between the compression plates at a pressure of 27 bar and at a temperature of 145 °C. The samples were left in the steel mold long enough to follow the vulcanization. Vulcanized compounds are marked with the prefix C.

**Table 1.** Chemical composition of standard reference and rubber compounds formulation prepared from leather waste.

Functions	Ingredients	Basic Additives			
		(% w/w)			
Rubber Additives	Natural Rubber (NR)	62.0			
	Zinc Oxide	3.1			
	Calcium Oxide	1.8			
	Stearic Acid	1.2			
	Sulfenamide	0.9			
	Calcium Carbonate	31.0			
	Total	100.0			
		BC (phr *)	CMPTD (phr)	CMCS (phr)	COT (phr)
Basic Compounds	Basic additives	100.0	100.0	100.0	100.0
Vulcanizing	Sulfur	2.0	2.0	2.0	2.0
Leather waste	MPTD	0.0	13	0.0	0.0
	MCS	0.0	0.0	13	0.0
	OT	0.0	0.0	0.0	13

\* Parts per hundreds rubber

All tests were performed in triplicate in order to calculate a standard deviation of measurements and provide the reproducibility of procedures employed.

### 2.2.1. Reinforced Rubber Compounds

Compounds containing MPTD and OT waste were re-prepared and reinforced with carbon black. This filler imparts strength and toughness to a rubber and also improves its resistance to tearing abrasion, and increases traction and durability. Carbon black not only improves the strength of the compound, but also influences the curing characteristics. Reinforced compounds are collected in Table 2 and marked with the prefix R.

In order to create fibers in the size range 2–20 mm PTD-waste was frayed (FPTD) by rag tearing (Rolando Machinery, RM8). In addition, an aliquot of milled PTD-waste was screened with a suitable sieve in the size range 0.5–2 mm (MPTD1). An important parameter for optimizing mechanical properties of rubber compounds is the percentage of leather-waste,  $\alpha$ , added to the basic compounds. To make this parameter evident, the value of  $\alpha$  is displayed as subscript of each formulation. Reinforced compounds and their composition, expressed as parts per hundred of rubber, are collected in Table 2.

**Table 2.** Reinforced rubber compounds prepared from leather waste.

Function	Ingredient	RBC (phr *)	RMPTD <sub>5</sub> (phr *)	RMPTD <sub>10</sub> (phr *)	RMPTD <sub>20</sub> (phr *)	RMPTD <sub>110</sub> (phr *)	RFPTD <sub>10</sub> (phr *)	ROT <sub>10</sub> (phr *)
Basic additives		100	100	100	100	100	100	100
Vulcanizing	Sulfur	2	2	2	2	2	2	2
Fillers	MPTD	0	6	13	28	0	0	0
	MPTD1	0	0	0	0	13	0	0
	FPTD	0	0	0	0	0	13	0
	OT	0	0	0	0	0	0	13
Carbon black		13	13	13	13	13	13	13

\* Parts per hundreds rubber

### 3. Mechanical Tests

#### 3.1. Static Mechanical Properties

##### 3.1.1. Tensile Strength

The test pieces are a dumbbell shape and were tested on a dynamometer (ADMET model). The tests were carried out at room temperature and, for each compound, three test repetitions were performed. Tests measure the force required to break a specimen and the extent to which the specimen stretches or elongates. In particular, tensile tests produced a stress–strain curve, from which one calculated the tensile stress,  $\sigma_b$ , and tensile elongation,  $\epsilon_b$ , corresponding to the rupture point and tensile stress at 300%,  $\sigma_{300}$ . All measurements were carried out in triplicate.

##### 3.1.2. Tear Resistance

The test to determine the tear resistance,  $\tau$ , was carried out to check the elastomers sensitivity to the tear propagation in case of cut damage. The measurement consists of indenting the sample with cuts of different dimensions and then subjecting the sample to a traction test. At the moment of tearing, an elongation  $\epsilon_\tau$  is reached. All measurements were carried out in triplicate.

#### 3.2. Dynamic Mechanical Properties

##### 3.2.1. Elastic Resilience

Elastic resilience,  $R_E$ , is the energy returned by the vulcanized sample when it is suddenly released from a state of strain or deformation. Measurements were performed with a Charpy's pendulum 20 min after vulcanization. This technique allowed measuring the energy absorbed in the process of fracturing the specimen. It is usually expressed as a ratio between the returned and applied energy of a moving mass, which impacts test pieces. For each specimen, the measurements were made in triplicate.

##### 3.2.2. Yertzley Resilience

The vibratory resilience was measured with the Yertzley Oscillograph. For each specimen the frequency of amplitude resonance,  $\nu_0$ , and the half-power width of the resonance curve,  $\Delta\nu$  (the difference between frequencies at which the amplitude is  $1/\sqrt{2}$  of the maximum) were measured, which yields

$$\frac{\Delta\nu}{\nu_0} = \tan \delta \quad (1)$$

The result obtained is rearranged as

$$Y_E = e^{-\pi \tan \delta} \quad (2)$$

which is Yertzley resilience measured by oscillograph. The variability between duplicate results on the same sample was of the order of  $\pm 5\%$  for the resonance.

### 3.2.3. Abrasion Resistance

The test is quite simple. Abrasion resistance is measured by moving a test piece of material across a surface of an abrasive sheet mounted on a revolving drum. Results were expressed as loss of mass,  $\Delta m$ . Each compound was subjected to three test replicates.

### 3.2.4. Shore Hardness Testing

Shore hardness,  $H$  (Shore A) was measured by durometer (Sauter GmbH version 1.2). The instrument utilizes an indenter loaded by a calibrated spring. Measurements were carried out at room temperature and replicated in triplicate. The penetration depth of the indenter under the load of 822 g (ShA) was measured. Shore hardness values may vary in the range from 0–100. Maximum penetration is 2.50–2.54 mm corresponding to Shore hardness 0. Maximum value 100 corresponds to zero penetration [26].

### 3.2.5. Plasticity Measurements

A shearing disc viscosimeter was used to measure the plasticity of crude rubber and its compounds. About 250 g of sample was placed in a chamber and preheated for one minute at 100 °C. The rubber compound was then trapped between the disc and walls of the cavity. At the end of the time the rotor was driven to 2 rpm and the resistance was measured after 4 min. The resulting value say  $x$ , termed Mooney viscosity, is reported as  $xML(1+4)100$ . All measurements were carried out in triplicate.

### 3.2.6. Vulcanization Kinetics

Compounding was performed in an open two-roll mixing mill where the ingredients and additives were added. Vulcanization rates were monitored with oscillating disk rheometer (Monsanto R100) at a temperature of 145 °C. The torque required for maintaining the oscillation amplitude is recorded. The times where torque takes the maximum, ( $t_{M_{max}}$ ), the minimum, ( $t_{M_{min}}$ ) and their differences,  $t_{\Delta M}$ , are important rheometric parameters to evaluate the progress of the vulcanization reaction. Usually, in the rubber industry, vulcanization is considered achieved when reaching the maximum torque. As usual in the rubber industry, we use the standard notation as  $t_{\alpha}$  to indicate the time scale needed for achieving  $\alpha\%$  of  $\Delta M$ . Cure rate index (CRI) values were calculated in accordance with

$$CRI = \frac{100}{t_{90} - t_{02}} \quad (3)$$

where  $t_{90}$  is optimum vulcanization time and

$$t_{02} = t_{M_{min}} + 0.2t_{\Delta M}$$

is the scorch time. All measurements were carried out in triplicate.

## 4. Morphology Analysis

### 4.1. Optical Microscopy

Optical micrographs were obtained by means of an optical microscope Optech B5 (Exacta + Optech Labcenter S.p.A., Modena, Italy) at 25 °C. In order to get representative results from the system, we used the video enhanced microscopy (VEM) technique. This technique combines the magnification power of the microscope with the digital image acquisition capability of a video camera (Panasonic, model GP-KR222).

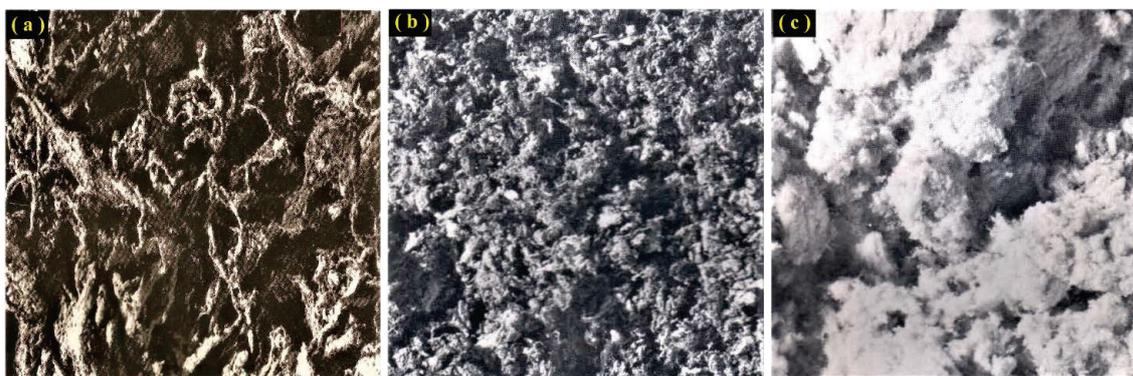
#### 4.2. Scanning Electron Microscope

The microstructure of fibers was investigated using scanning electron microscopy (Leica Stereoscan 100). Small pieces of fiber were fixed vertically on an aluminum stub using conductive glue. A sputter coater (Dynavac) was used for coating a thin layer of gold on the cross section and side wall of the fibers. A digital Cambridge/Leica Stereoscan 100 Scanning Electron Microscope (SEM) with filament using 25 kV of acceleration tension for morphological studies of the fibers.

### 5. Results And Discussion

#### 5.1. Optical Microscopy Investigation

Rubber product quality depends on how finely the different compounds are mixed. Therefore, properties such as geometric shape, size and surface area of individual particles play a fundamental role in determining the final characteristic of rubber artifacts. On this basis, several specimens of each sample were examined by optical microscopy. Results are shown in Figure 1, where shredded and non-shredded PTD samples are compared. In Figure 1a, for the non-shredded sample, one can notice the presence of large cavities and badly mixed pieces of fiber. In shredded samples, Figure 1b, fibers are finely dispersed so that a high surface area is developed. The photograph in Figure 1c shows the very soft, wadding-like morphology of the OT sample. This softness of the OT sample is the result of its high porosity. Indeed, the OT sample is oil tanned with cod-liver fish oil, and stocked into dried hide until they have replaced the natural moisture of the original skin. Blended oils and greases are then incorporated into the leather to lubricate it and to enhance its softness.



**Figure 1.** Morphology of leather waste used to prepare rubber compounds. (a) post-tanning dyeing (PTD) non-shredded sample; (b) PTD shredded sample; (c) oil tanning (OT) sample.

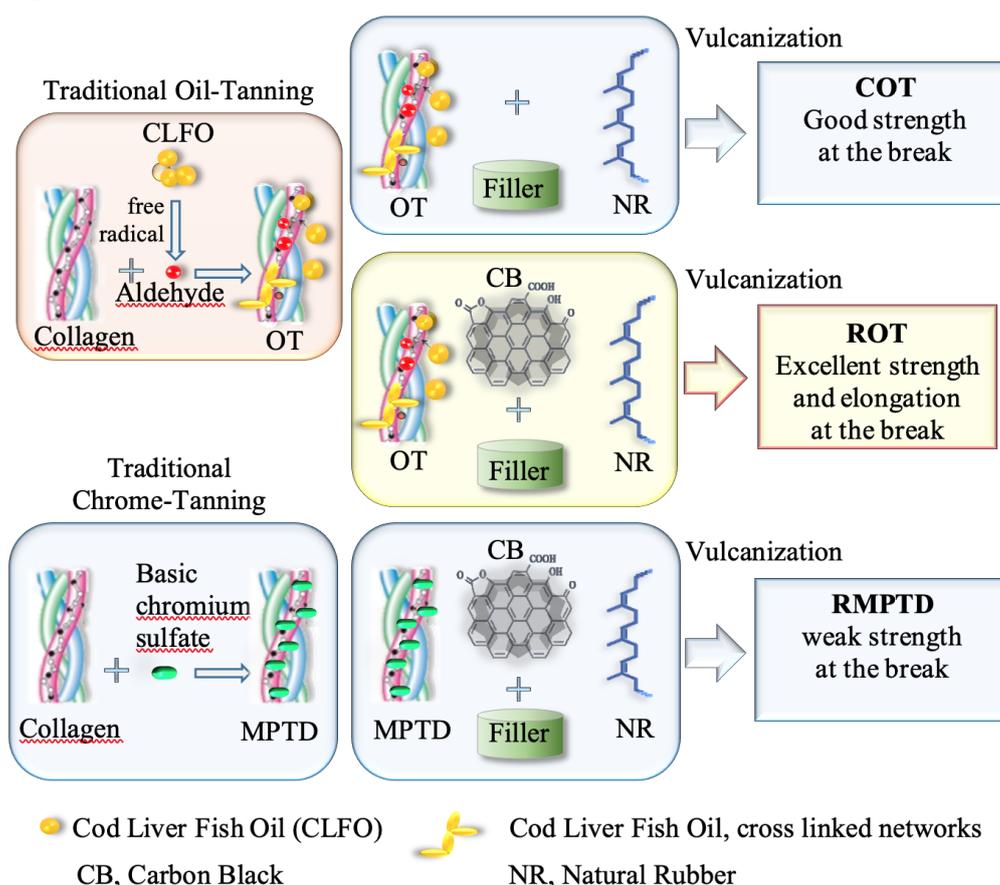
#### 5.2. Vulcanization Characteristics

By vulcanization, we mean a set of chemical reactions that convert NR into cross-linked elastomers. CMPTD, CMCS, COT samples and the reference formulation BC were vulcanized and the set of reactions rheometrically monitored. Studied parameters include  $t_{02}$  as scorch time,  $t_{90}$  as final vulcanization time,  $\Delta M$  as cross-link density,  $R_E$  as absorption of energy and  $\rho$  as material compactness, experimental results are collected in Table 3. As can see, all formulations exhibit  $t_{02}$  and  $t_{90}$  significantly lower than BC (especially the COT sample), indicating that leather waste performs the action of the accelerator. Collagen is a fibrillary protein, which also contains sulfurous amino acids such as cystine and methionine, therefore it is a source of additional sulfur. As soon as temperature exceeds 140 °C, sulfur released by amino acids is added to the vulcanization sulfur, hence the process takes place with higher sulfur content. Consistently, all formulations display a greater CRI than BC reference. From inspection of Table 3 one finds that  $\Delta M$ , for CMTPD and CMCS compounds, is slightly lower than BC while for the COT formulation it turns out to be significantly lower than BC. The introduction of essential main chain modification reduces the resilience. Thus, data in Table 3 indicate that in all formulations the leather waste introduces modifications along the polymer chains, resulting in a

lower  $R_E$  value, compared to BC. CMPTD and CMCS compounds exhibit reactivity and mechanical properties similar to each other, but quite different from COT (see Table 3 and Figure 3). The different behavior is due to the specific tanning processes: fish oil for COT and chromium for PTD and CS waste. The two types of tanning are illustrated in Figure 2. In OT trimmings, a fraction of the unreacted tanning oil remains free, oil that can be solvent-extracted from the tanned leather (Figure 2). Although the action of tanning oil on collagen is not yet fully clarified, it is well-known that the oil reacts with some proteins to form aldehydes reacting with collagen [27]. During oxidation, the oil polymerizes to form a film adhering to the fibers increasing probability of creating cross-linked networks, as illustrated in Figure 2.

**Table 3.** Characteristic parameters of vulcanization curves of rubber compounds obtained from leather waste. Experimental error for each value is calculated as standard deviation of repeated measurements.

Compounds	$t_{02}$ (s)	$t_{90}$ (s)	$\Delta M$ (Nm)	$CRI$ ( $s^{-1}$ )	$\rho$ $kgm^{-3}$	$R_E$ (%)
BC	131 ± 12	678 ± 65	3.3 ± 0.3	0.18 ± 0.01	1260 ± 25	80 ± 4
CMPTD	115 ± 11	504 ± 48	3.7 ± 0.4	0.26 ± 0.02	1260 ± 25	74 ± 4
CMCS	122 ± 12	534 ± 51	3.8 ± 0.2	0.24 ± 0.01	1270 ± 25	70 ± 3
COT	106 ± 10	492 ± 47	2.8 ± 0.2	0.27 ± 0.01	1250 ± 25	72 ± 4



**Figure 2.** Schematic illustration of the fabrication process involving a cross-linking reaction between leather collagen fibers and natural rubber (NR), in which carbon black serves as cross-linker

### 5.3. Static Mechanical Properties

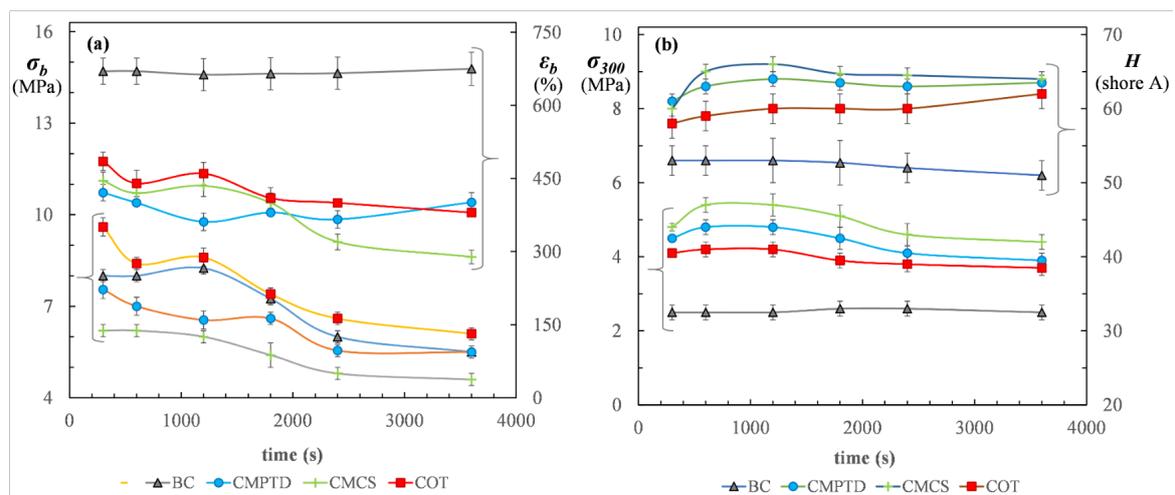
Generally, vulcanization reaction reach a maximum and start to decrease, resulting in weaker mechanical properties for longer curing times. This *reversion* phase is due to the breakdown of some

unstable polysulfidic cross-links formed in the vulcanization step leading to deterioration of physical properties. In industrial practice, the vulcanization process lasts for long times, then, in order to understand the influence of the reversion on the mechanical properties of formulations based on NR with the incorporation of leather waste, the vulcanization effect was monitored for a time exceeding the optimum value.

Figure 3a shows  $\sigma_b$  and  $\epsilon_b$  vs. the vulcanization time, for CMPTD, CMCS and COT compounds. For comparison,  $\sigma_b$  and  $\epsilon_b$  of the reference BC, measured under the same experimental conditions, have also been plotted. It is immediately seen that compounds, except COT, exhibit a  $\sigma_b$  lower than BC. As regards the elongation at the rupture point, all compounds display  $\epsilon_b$  lower than BC. Furthermore, COT formulation shows a  $\sigma_b$  value significantly larger than BC.

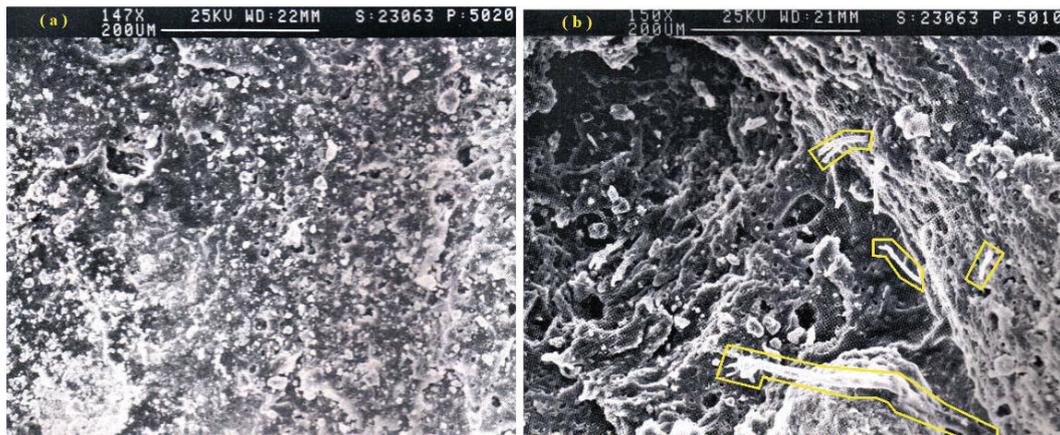
Figure 3b shows  $\sigma_{300}$  and  $H$  (shore A) vs. the vulcanization time. All the formulations investigated have values of  $\sigma_{300}$  and  $H$  (shore A) greater than BC. In addition,  $\sigma_{300}$  decreases over time. This means that subjected to the same stress CMPTD, CMCS and COT compounds extend less than BC reference, therefore, in working conditions, these materials undergo less elongation. This is consistent with the literature [28], in which NR-based compounds with the incorporation of leather waste were found to have a significantly lower breaking load and a strong increase in hardness. Hence, it can be inferred that chrome-tanned leather waste like PTD and CS are suitable for manufacturing floors mats, soles and heels, while the COT compound can be used for making hose or conveyor belts where a greater tensile strength is required.

The increased hardness of the compounds was further investigated by monitoring the vulcanization of CMPTD and BC compounds via SEM.



**Figure 3.** Vulcanization rates for CMPTD, CMCS and COT compounds. (a) Breaking load and elongation-at-break vs. vulcanization time; (b) load at 300% and hardness  $H$  (Shore A) vs. vulcanization time. Experimental results of the reference BC compound is plotted for comparison. Error bars indicate the standard deviation of repeated tests.

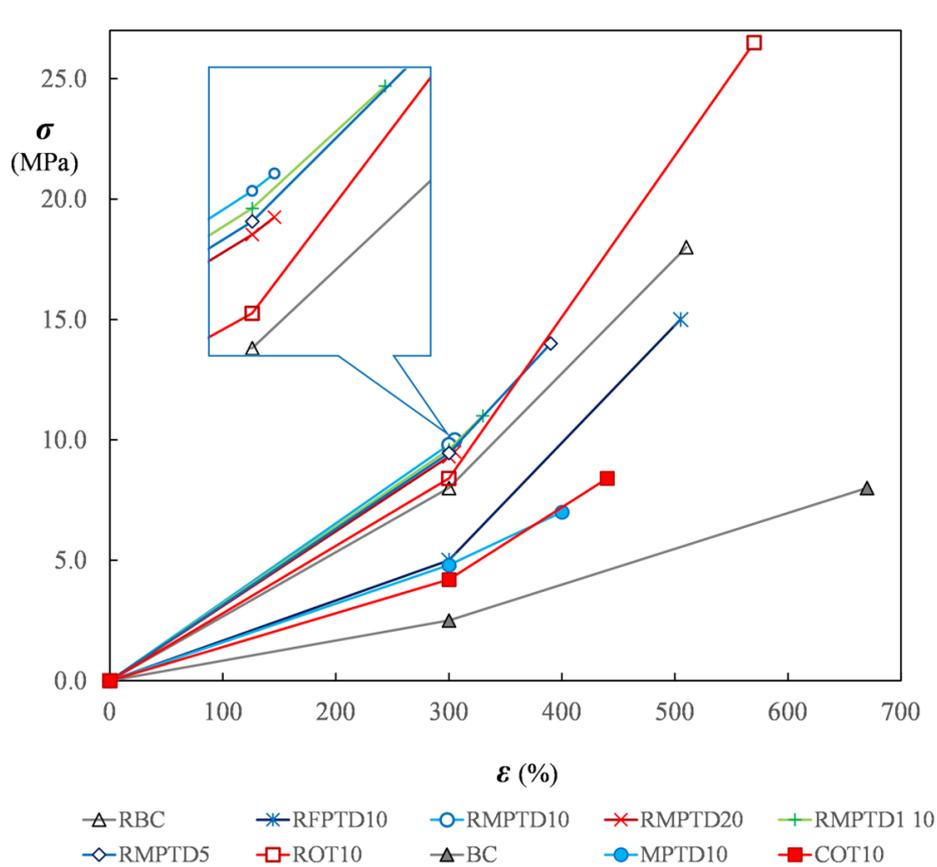
Figure 4 illustrates the SEM micrographs of the flexural fractured surface of CMPTD and BC compounds, immediately after vulcanization. Inspection of Figure 4b shows that the polymeric matrix incorporates some partially melted and vitrified fibers. It is well-visible that a large fiber and many small fibers are emerging from the matrix, as highlighted by the yellow contour. Likely, the persistence of the CMPTD compound, for a long time, at high temperature leads to melting and vitrification of crystalline regions.



**Figure 4.** SEM images of rubber compounds. (a) Sample BC immediately after vulcanization; (b) sample CMPTD immediately after vulcanization. Yellow lines highlight fibers emerging from the matrix.

#### 5.4. Reinforced Materials

Experimental results discussed above have revealed that the CMCS sample exhibits slightly more favorable mechanical performance than the CMPTD sample, such as the hardness which is a highly appreciated parameter for the products herein investigated. However, PTD waste is produced by leather industries in greater quantities. Furthermore, due to its chemical constitution PTD-waste must only be disposed of in landfills. Based on these considerations, formulations containing MPTD and OT waste were reinforced with carbon black. The reinforcing agent develops a high surface area, increases tensile strength and hardness (shore A) [29,30] favoring the interactions between fiber-waste and polymer matrix. Thus, compounds were vulcanized in the presence of carbon black and hardness shore A monitored as the vulcanization proceeded. A direct comparison between reinforced and non-reinforced compounds reveals that both RBC and all reinforced samples undergo a hardness increase of about 10 *H*-unit and resilience RE around 60%. As expected, the carbon black compacts the collagen fibers and the hardness of the material grows. A careful inspection of Figure 5 reveals that mixtures containing a constant waste concentration, but a different fiber-length, namely RMPTD<sub>10</sub>, RMPTD<sub>10</sub> undergo only a slight change in the mechanical properties, while RFPTD<sub>10</sub> (2–20 mm fibers) has a rather different behavior. In particular, the RFPTD<sub>10</sub> compound has lower  $\sigma$  and  $\sigma_b$  than RBC, furthermore  $\epsilon_b$  is significantly larger. Usually, the incorporation of fibers into NR causes an increase in  $\sigma$  and  $\sigma_b$  with a corresponding decrease in  $\epsilon_b$ . To explain this unusual behavior, it must be borne in mind that both the texture of the leather and the three-dimensional structure of collagen-fibers contribute to the mechanical properties of these materials. In other words, texture-relaxation and collagen-stretching cooperate for the mechanical properties of the composite material. Generally, plastic relaxation of texture is the predominant effect, however if the sample is reduced to a sufficiently small size, the relaxation effect is negligibly small and collagen-fiber stretching prevails. Thus, results displayed in Figure 5 indicate that RFPTD<sub>10</sub> compound-sizes are such that the texture relaxation strongly influences the values of  $\sigma$  and  $\epsilon_b$ . This aspect is particularly useful in the footwear industries, where shoe uppers must be manufactured to provide comfort by adapting to different shapes of feet. Table 4 reveals that for formulations with increasing fiber content (RMPTD<sub>5</sub>, RMPTD<sub>10</sub>, RMPTD<sub>20</sub>), several mechanical parameters vary very little for fiber concentrations higher than 10%. This implies that, where they can be used as materials, large quantities of leather waste will be disposable.



**Figure 5.** Load-versus elongation curves obtained in tensile tests for leather waste-NR. Experimental results of reinforced and non-reinforced compounds are plotted for comparison.

Furthermore, from Table 4 it is evident that ROT<sub>10</sub> compounds exhibit the lowest Mooney viscosity. This is because fish oil, present only in these cutouts, performs a lubricating function. Mechanical properties similar to those of CMPTD and RMPTD compounds were obtained by Ruiz ([31]) through chemical pretreatments and use of compatibilizers. For the ROT compound,  $\sigma_b$  and  $\epsilon_b$  are greater than for RBC. Once again there is unusual behavior, however the OT fibers are now very small in size, so that the resulting effect cannot be explained by the texture-size. Indeed, the comparison between the various samples, as illustrated in Figure 2, suggests that carbon black activates and accelerates a strong collagen fiber-NR-tanning oil interaction. The OT sample still contains 3–5% of fish oil in the free form (removable by solvent). Obviously, to establish the exact mechanism of the fish oil-collagen and collagen-NR interactions, a detailed mechanistic investigation must be carried out. Here, experimental values were compared with equivalent results, obtained on similar systems where the interaction mechanism was known. In particular, investigating the role of fish-oil in the tanning activity, it was found that the polyunsaturated fats of the oil, at 70–80 °C, self-oxidize generating aldehydes [27]. Polyunsaturated aldehydes produced bind covalently to the amino group of collagen, by a Schiff base arrangement and simultaneously an H-bond is established with the carboxyl-groups of the collagen. Thus, a cross-connection of oxidized oil and collagen is generated. As regards collagen-NR interaction, a recent study on vulcanization with triethoxyvinylsilane as a cross-linker showed the formation of a covalent cross-linking between the C=C in triethoxyvinylsilane and C=C in the NR molecular chain [22]. In addition, NR cured with collagen and triethoxyvinylsilane behaves mechanically like the ROT compound. Therefore, by chemical similarity, one may infer that a synergistic function is activated by carbon black. Namely, double bonds of the fatty acids in cod liver fish-oil during the vulcanization process bind both to collagen and to the polymeric matrix forming a three-dimensional network. Such a 3D structure is a texture capable of making explicit the singular observed property.

**Table 4.** Mechanical characteristics of reinforced rubber compounds. Experimental error for each value is calculated as standard deviation of repeated measurements.

Specimen	Viscosity ML(1+4)100	$\sigma_b$ (MPa)	$\epsilon_b$ (%)	$\sigma_{300}$ (MPa)	$Y_E$ (%)	$\tau$ (kNm <sup>-1</sup> )	$\epsilon_\tau$ (%)	$\Delta m 10^6$ kg
RBC	62 ± 4	18.0 ± 0.2	510	8.0 ± 0.4	74 ± 4	144 ± 17	360 ± 7	139 ± 7
RFPTD <sub>10</sub>	70 ± 4	15.0 ± 0.1	505	5.0 ± 0.2	52 ± 3	49.0 ± 6	220 ± 5	252 ± 13
RMPTD <sub>10</sub>	68 ± 4	10.0 ± 0.1	305	9.8 ± 0.5	61 ± 3	99 ± 12	210 ± 4	181 ± 9
RMPTD <sub>20</sub>	73 ± 5	9.5 ± 0.1	305	9.3 ± 0.5	57 ± 3	92 ± 11	200 ± 4	225 ± 11
RMPTD <sub>10</sub>	66 ± 4	10.5 ± 0.1	330	9.6 ± 0.5	61 ± 3	107 ± 13	220 ± 5	178 ± 9
RMPTD <sub>5</sub>	62 ± 4	14.0 ± 0.1	390	9.5 ± 0.5	64 ± 3	178 ± 21	240 ± 5	162 ± 8
ROT <sub>10</sub>	57 ± 3	26.5 ± 0.3	570	8.4 ± 0.4	62 ± 3	109 ± 13	300 ± 6	184 ± 9

## 6. Manufacturing of Rubber Artifacts Based on Chromium-Tanned Waste and Monitoring of Chromium Release

In previous sections we have discussed the properties of elastomers produced from compounds leather-waste-based and we outlined the way they may be used to manufacture artifacts of great rigidity and hardness. We now consider materials fabricated by industrial presses from RMPTD<sub>10</sub> and resistant to both strong static and dynamic stresses.

### 6.1. Artifacts Resistant to Static Stresses

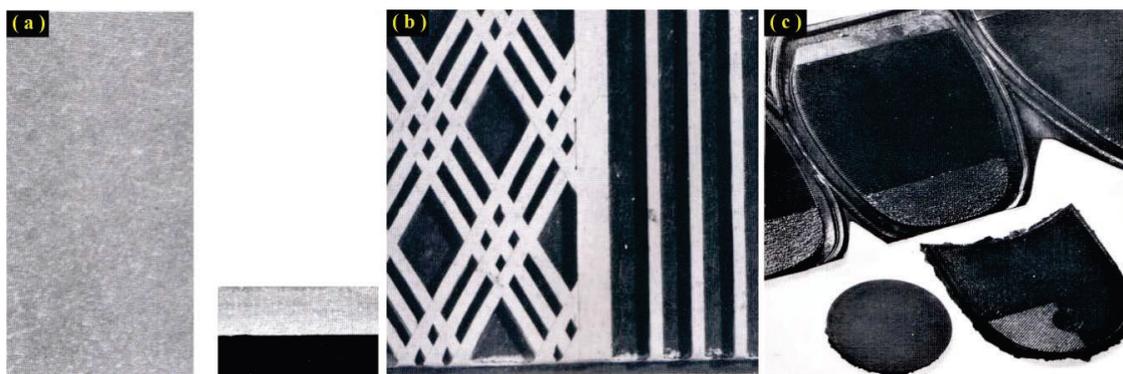
Such property makes them especially attractive for manufacturing laminate floor coatings, where several layers are pressed together to form a highly resistant composite *laminate* material, the upper layer is shown in Figure 6a. The finished laminate is then glued onto a backing layer and cut into sections with exact dimensions. In order to install these laminate flooring in accordance with accepted tolerances within the flooring industry, sub-floors have to be prepared. The laminate support was made of the same elastomeric material and is shown in Figure 6a (black layer). The perfect adherence between the support and the laminate makes the material suitable for constructing base supports for flooring. The formulation was also used to manufacture car mats (Figure 6b). Both of these artifacts were manufactured with formulations containing 10 wt% of leather waste.

### 6.2. Artifacts Resistant to Dynamic Stresses

Soles and heels are the bottom part of the footwear in direct contact with the ground, the main parts that protect the sole of the foot and are subject to constant stresses. Figure 6c shows soles and heels for shoes and anti-slip rubber grip for chairs. Such artifacts were manufactured with formulations containing 10 wt% of leather waste. Our drag test and gait trial results obtained on a stainless steel floor surface wet with glycerol solution indicated that the newly developed rubber showed good slip resistance. It is worth pointing out that to prevent the formation of bubbles, the samples were prepared in a suspension of calcium oxide (Calaxol).

Such artifacts are currently prepared using 20 wt% of *micronized* cellulose so that they have to be sold at high prices or not produced. The proposed formulations, with 20 wt% of leather waste instead of microcellulose, would reduce costs and widen the market segment. Many plastic materials are generated in the world and, moreover, several tons of leather waste have to be disposed of, then resulting economic and environmental benefits are considerable.

The use of tanned material, could cause embarrassment in the consumer who unconsciously associates the high amount of leather-waste with the pollution caused by chrome tanning. For this reason, a certain number of samples were subjected to cessation tests, according to the European Regulation [32]. For all tests, carried out after one year of product life, the Cr(VI) concentration was below the instrumental detection limits [33,34], indicating no aging effect.



**Figure 6.** Products manufactured from RMPTD<sub>10</sub> formulation. (a) Laminate floor covering. The white surface is the top layer, the black band is the backing layer; (b) car floor mat; (c) soles and heels for shoes and anti-slip rubber grip for chairs.

## 7. Conclusions

The rising interest in the valorizing of industrial by-products is one of the main reasons for exploring different separation methods of leather waste along the production-chain in the tanning industry. Recently, we showed that through a detailed and accurate separation of waste, during leather processing, an optimal zero-waste condition may be attained [25]. The main reason that led to this success is that the tanned leather waste raw material was made economically advantageous for other production cycles. The advantage is to avoid the expensive and complex pretreatment of waste, some of which must be disposed of in landfills. Consequently, the mechanical and chemical properties, linked to the structural complexity of the leather, have been preserved allowing for a wider spectrum of uses. Three types of waste, corresponding to three different stages of skin leaching, i.e., PTD, CS (chrome tanning) and OT (cod liver oil tanning), were used as fiber-fillers for vulcanizing NR. The study of the vulcanization process indicates such fibers produce an accelerating effect, especially noted for OT-waste. The mechanical tests performed on compounds show a reduction of the tensile strength of materials in working conditions and an increased hardness, especially in the compounds containing PTD and CS fibers. Therefore, the compounds can be usefully used for the production of flooring supports, soles and heels for shoes and anti-slip rubber grip for chairs. Mixtures obtained with OT fibers, exhibit also a significant increase in  $\sigma_b$ . Generally, compounds can be used as materials with functions requiring greater tensile strength (e.g., hoses, conveyor belts). In order to further increase the characteristics of hardness and breaking strength, the mixes are reinforced with carbon black. Usually, the incorporation of carbon black into NR causes an increase in  $\sigma$  and  $\sigma_b$  with a corresponding decrease in  $\epsilon_b$ . While for PTD and fibers, expected results were recorded, for OT fiber, on the contrary, there was a strong increase in both  $\sigma_b$  and  $\epsilon_b$ , compared to the reference compounds.

Thus, experimental results show that leather waste can be used, without any pretreatments, to manufacture products destined for different uses. Herein, as an example, formulations containing 10wt% of PTD waste were used to manufacture car mats and floor laminate supports; while formulations with 10 or 20% of PTD were used to make soles and heels for shoes and anti-slip rubber grip for chairs. Leather waste was used without chemical treatments so that the release of chromium could be aroused. In this regard, both the formulations and the artifacts were monitored for the release of chromium (VI) traces [28,31]. However, concerns about possible synergistic harmful effects between rubber and tanned waste (e.g., chromium release) [35] have prompted us to carry out chemical analyses for a whole year [33,34]. Results showed that the amount of Cr(VI) was below the instrumental detection limits, indicating that this metal is either absent or according to the European Regulation less than 5 mg per kg of product [32]. The examples presented in this research seem to confirm the idea that efficient waste separation and their proper use lead to a twofold advantage. On the one hand, the environmental impact of tanneries is reduced, while, on the other hand, leather industries have, with the waste, an alternative source of gain.

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