SURFACE MODIFICATION OF RUBBER FROM END-OF-LIFE TIRES FOR USE IN CONCRETE: A DESIGN OF EXPERIMENTS APPROACH

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ABSTRACT

A large amount of discarded tire waste generated year after year has encouraged the scientific community to seek alternatives for recycling or reusing this waste. The cross-linked nature and the high number of additives in tires make recycling significantly difficult. Thus, the use of particulate rubber as filler for other materials such as concrete has emerged as an attractive alternative. However, the hydrophobic nature of the rubber and hydrophilic particles of cement decreases the compatibility at the cementitious matrix-rubber interface, affecting the concrete's final performance. This work presents a method based on hydrogen peroxide and Fenton for the oxidation of rubber particles from end-of-life tires to introduce hydrophilic groups on the surface of the particles to improve compatibility at the interface. The method was studied from an experimental design approach based on the infrared spectroscopy response and using a Rechtschaffner Resolution V design, PCA and PLSR in order to evaluate variables such as time, temperature and reactants. The concentration of H_2O_2 and reaction temperature was shown to increase the oxidation, while Fenton reduces the time of oxidation.

Keywords: Rubber, tires, concrete, peroxide oxidation, Fenton.

1. INTRODUCTION

Rubber is an elastomeric polymer composed by repeating isoprene units. Natural rubber is extracted from the latex of the *Hevea brasiliensis* tree, which is grown in plantations in tropical regions of Southeast Asia[1]. The structure of natural rubber is mainly poly(*cis*-1,4-isoprene), a polymer with a high molar mass, mixed with 2-4% of protein matter, 1-4% of resins, fatty acids, and other compounds[2].

Other elastomeric compound is the synthetic rubber which corresponds to polybutadiene and it is used as a substitute for natural rubber due to its excellent chemical resistance to acids, mineral oils, gases, and other substances[3]. After manufacture, synthetic rubber is vulcanized through the formation of disulfide bonds. There are many types of synthetic rubber with different physical and chemical characteristics. Among the most widely used synthetic rubbers are styrene-butadiene, ethylene-propylene, and silicone rubbers. The elastomeric properties of rubber along with their chemical resistance, is used in countless applications in the industrial sector, such as in tires, footwear, pipes, transmission belts, or parts for fluid sealing[4].

Consequently, the generation of rubber waste has become a global concern due to its negative impact on the environment and human health. Undoubtedly, the most important source of rubber contamination is end-of-life tires. It is estimated that around 1 billion tires are withdrawn from use each year, 1000 million tires reach the end of their useful life every year. By the year 2030, the number can reach up to 1200 million tires representing almost 5000 million tires[5]. Unfortunately, their cross-linked nature and the high content of additives difficult their recyclability (see table 1).

Table 1. Composition of rubber tires[6].

Substance	Concentration (wt%)
Rubber (natural and synthetic)	51
Reinforcing agent (carbon black, silica)	25
Softener (petroleum oil and resins)	19.5
Vulcanizing accelerator (thiazole compounds)	1.5
Vulcanizing agent (sulphur, organic vulcanizers)	1.0
Others[a]	2

[a]vulcanizing accelerators aid, fillers, antioxidant, etc

An alternative to reduce the volume of unused rubber is to use rubber particles as fillers. In this sense, it has been used in athletics tracks, thermal insulation, road drainage systems, and construction, among others[7-15]. Using rubber waste in this type of application represents, in addition to the important environmental and economic advantages, improvements in the performance of this type of products, such as increased impact resistance and fatigue resistance. However, these advantages also entail the problem of loss in properties such as elastic modulus and compressive strength.

One of the most promissory applications of end-of-life rubber particles is as filler in asphalt mixtures[7]. Two methods are used for this application: i) wet and ii) dry method. The first method consists of mixing the particulate rubber and the asphalt binder at high temperature in a high-cut mixer, for its later use as bitumen within the asphalt mixture. In this system, the rubber works as a modifying agent, having as a result product what is commonly called asphalt-rubber, which is applied in the same way as a conventional modified binder. The wet manufacturing procedure can be carried out in two ways: in the first case, called refinery process, the rubber-based asphalt is made at the asphalt-producing plant, subsequently transported to the terminal to be combined with the aggregates and produce the asphalt mix. In the second case, called "on the ground", the asphalt is modified on the same asphalt plant, then incorporated into the aggregates in the mixing process. The second method is based on introducing the rubber powder directly into the mixer of the asphalt plant, and as one more component of the mixture, however, it is first necessary to mix it with the aggregate to achieve its total distribution and thus increase its temperature, before adding asphalt cement. In this process, the rubber powder acts as an aggregate. Still, its finest particles interact with the asphalt cement, modifying their properties and improving the asphalt mixture's performance.

On the other hand, concrete is the most widely used construction material worldwide[16]. In this way, recycling end–of–life rubber and incorporating it into concrete material is very attractive from an environmental point of view[17]. The incorporation of rubber particles in concrete can increase energy absorption under dynamic load[18], increase impact resistance[19], improve resistance to freeze-thaw cycles[20], increase acoustic and thermal insulation[21], and reduce noise[22]. However, even though progress has been made in the study of the incorporation of recycled rubber into concrete, there are still several challenges that need to be addressed in a multidisciplinary way to deliver comprehensive solutions that are technically feasible, cost-effective and sustainable.

One of the main troubles is that rubber particles has low compatibility with inorganic materials, such as concrete. Cement paste is a hydrophilic material, while the surface of the crumbled rubber is hydrophobic. This loss of compatibility at the cementitious matrix-rubber interface has consequences on the material's final performance. One method of improving rubber in concrete is to treat the surface of the rubber particles to improve compatibility, which involves incorporating hydrophilic functional groups, altering surface properties, and potentially enhancing adhesion between the rubber particles and cement.

The objective of this research is to modify rubber particles from tires that are no longer in use through and oxidation reaction with peroxide oxidation and subsequent Fenton reaction. The process variables were evaluated by design of experiments (DoE). Principal component analysis (PCA) and partial least squares regression (PLSR) were used in order to correlate the effect of each process variable on rubber modification.

2. EXPERIMENTAL PART

Particulate rubber was kindly provided by PolAmbiente (diameter 2-4 mm), hydrogen peroxide 50% was kindly provided by Solvay-Peróxidos (Chile), iron sulfate (Sigma-Aldrich).

2.1 Oxidation with peroxide and Fenton

A 14 experiments Rechtschaffner Resolution V design was carried out in order to study four X-variables involved in the rubber modification process. For this purpose, the rubber was contacted with a hydrogen peroxide solution (X_1), stirring at 150 rpm at a given temperature (X_2) and for a given time (X_3). Then, the rubber was filtered and dried for 3 h at 50 °C. In addition, a Fenton reaction (X_4) with the rubber was evaluated by contacting $FeSO_4$ with the hydrogen peroxide solution in the first step. The Fenton reaction has a Fe^{2+}/H_2O_2 mass ratio of 1:10 at pH 3.0 – 3.4 for a time of 30 minutes at 300 rpm. Finally, it was filtered and dried for 3 h at 50 °C. Table 2 summarizes the X-variables and the ranges studied in this method. A PCA and PLSR was performed on the DoE experiments in order to obtain the best conditions for maximizing the rubber surface modification. DoE and PLSR regression were carried out by using MODDE Pro 12® software (Sartorius Stedim Biotech, Sweden). PCA was carried out by using SIMCA 16.0.1® software (Sartorius Stedim Biotech, Sweden).

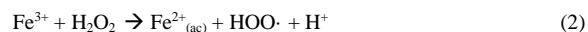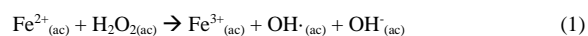**Table 2.** Variables studied in the Rechtschaffner Resolution V design.

Variable	Abbreviation	Levels	
		(–1)	(+1)
X_1, concentration of H_2O_2 (wt%)	H_2O_2	25	50
X_2, temperature for reaction with H_2O_2 (ºC)	Temp	60	80
X_3, time for reaction with H_2O_2 (min)	Time	30	60
X_4, Presence of Fenton reaction	$FeSO_4$	No/Yes	

2.2 Physicochemical characterization

The rubber samples were analyzed before and after the treatments through coupled infrared spectroscopy with attenuated total reflectance (FTIR-ATR) in an instrument Nicolet iS10, Thermo Scientific. A background spectrum was first applied to eliminate absorption bands of gases such as CO_2, humidity or traces of solvents that interfere with the IR spectrum of the sample. Then, the sample is deposited on the glass to obtain the IR spectrum, it should be noted that an experiment is performed in triplicate. Finally, the rubber samples were analyzed using scanning electron microscopy (JEOL modelo JSM-6380) and dispersive energy X-ray diffraction (EDX). The samples coated with gold under reduced pressure (SPI-Module sputter coater) to determine the elemental composition of C, O and S on the surface of the particles to 10 images. Statistical analysis of One-Way ANOVA was performed using Prism 8 (GraphPad, USA)

3. RESULTS AND DISCUSSION

This method consisted of oxidizing the rubber surface through a strong oxidant such as hydrogen peroxide and then complementing this oxidation with a Fenton reaction (see Eq 1-2). For poly(isoprene) rubber, the peroxide oxidation mechanism occurs in the double bond of the repetitive unit, passing to an epoxide group and subsequently to a diol[23]. Similarly, the Fenton reaction produces hydroxyl radicals, with a more oxidizing strength, that can cause cleavage of double bonds to form alcohols or cause homolytic cleavage of single C-C bonds to produce terminal hydroxyls[23].

$$Fe^{2+}_{(ac)} + H_2O_{2(ac)} \rightarrow Fe^{3+}_{(ac)} + OH\cdot_{(ac)} + OH^-_{(ac)} \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+}_{(ac)} + HOO\cdot + H^+ \qquad (2)$$

Table 3. Experiments and the measured responses for the Rechtschaffner Resolution V design of experiments.

Exp[a]	X_1 H_2O_2 (wt%)	X_2 Temp (ºC)	X_3 Time (min)	X_4 $FeSO_4$	Y_1 838 (cm^{-1})	Y_2 964 (cm^{-1})	Y_3 1050 (cm^{-1})	Y_4 1130 (cm^{-1})	Y_5 1540 (cm^{-1})	Y_6 1650 (cm^{-1})	Y_7 2850 (cm^{-1})	Y_8 2920 (cm^{-1})	Y_9 3580 (cm^{-1})
1	25	60	30	No	0.1158	0.1180	0.1317	0.1262	0.0996	0.0755	0.0683	0.0800	0.0383
2	25	80	60	Yes	0.1055	0.1036	0.1156	0.1072	0.0652	0.0624	0.0506	0.0603	0.0251
3	50	60	60	Yes	0.1377	0.1390	0.1420	0.1340	0.0768	0.0732	0.0520	0.0623	0.0230
4	50	80	30	Yes	0.1817	0.1747	0.1790	0.1663	0.1125	0.1060	0.0718	0.0781	0.0402
5	50	80	60	No	0.1863	0.2124	0.2000	0.1947	0.1355	0.1270	0.1032	0.1108	0.0718
6	50	80	30	No	0.1624	0.1695	0.1507	0.1422	0.1058	0.0966	0.0860	0.1030	0.0371
7	50	60	60	No	0.1617	0.1600	0.1520	0.1423	0.1134	0.1051	0.0907	0.1029	0.0481
8	50	60	30	Yes	0.1377	0.1403	0.1427	0.1350	0.0883	0.0830	0.0596	0.0695	0.0306
9	25	80	60	No	0.1823	0.1950	0.1733	0.1637	0.1327	0.1222	0.1024	0.1146	0.0593
10	25	80	30	Yes	0.1620	0.1621	0.1521	0.1428	0.1075	0.0977	0.0788	0.0932	0.0358
11	25	60	60	Yes	0.1075	0.1011	0.1147	0.1098	0.0690	0.0615	0.0439	0.0552	0.0175
12	37.5	70	45	No	0.1573	0.1527	0.1573	0.1480	0.1170	0.1083	0.0926	0.1052	0.0533
13[b]	37.5	70	45	No	0.2020	0.2140	0.1927	0.1810	0.1497	0.1373	0.1096	0.1207	0.0658
14	37.5	70	45	No	0.1423	0.1357	0.1330	0.1250	0.1071	0.0973	0.0798	0.0910	0.0419

[a] experiments performed in random order
[b] outlier data

The infrared spectra of the 14 experiments are presented in Figure 1. Main changes in the region of 900–1250 cm^{-1} and 3000 – 3500 cm^{-1} are observed.
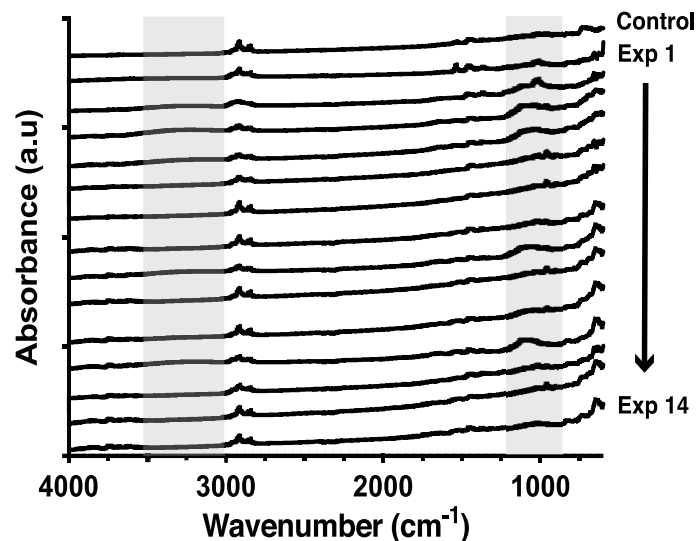

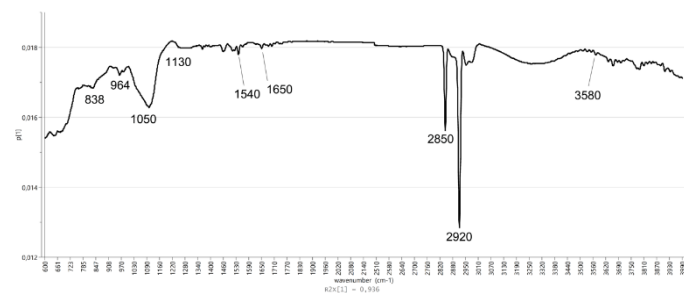**Figure 1.** FTIR-ATR spectra of the DoE (14 experiments).

Figure 2. Loading plot (first PCA-component) for the second derivative of the FTIR-ATR spectra.

A PCA analysis of the infra-red spectra for the 14 experiments ($R^2 = 0.999$; $Q^2 = 0.997$) compared with the unmodified rubber (UMR) was performed. According to the loadings plot of the first PCA-component, the bands of the infrared spectrum that showed the most significant variation were: 838; 964; 1050; 1130; 1540; 1650; 2850; 2920 and 3580 cm^{-1} (Figure 2). The PCA scores plot (Figure 3a) shows that the first component divides the experiments performed with and without Fenton reaction. The second component divides the UMR and the modified experiments. The experiment 4 is the further away from the UMR, indicating that has the more pronounced modification.

Figure 3b shows a loading scatter plot of the *X*- and *Y*-weights (*w* and *c* respectively) for the PLS interaction model ($R^2 = 0.868$; $Q^2 = 0.655$ with 3 PLS-components) obtained from the DoE which presents the relationship between *X*-variables and *Y*-responses in a single overall plot. The *Y*-responses 1650 and 1540 corresponding to bands C-C double bonds are negatively correlated with the presence of FeSO$_4$ (*X*$_4$) in the reaction. Also, the *Y*-response 838 that could indicate C-H stretching for carbons with double bond decreases when FeSO$_4$ is used in the reaction. These relationships indicate that including the Fenton reaction in the process, these IR signals decrease, so more cleavage of this bonds are reached, and thus more oxidation is achieved on the rubber surface. The *X*-variables concentration of H$_2$O$_2$ (*X*$_1$) and temperature of reaction with H$_2$O$_2$ (*X*$_2$) are positively correlated with bands 1050 and 1130 which indicate that when these variables are set in their highest level (+1) the signal C-O of alcohol increases, so the oxidation process is increased.

The *X*-variable time of reaction with H$_2$O$_2$ (*X*$_3$) is not significant ($p > 0.05$) but has an important interaction with FeSO$_4$ ($p < 0.05$). This interaction time×FeSO$_4$ is located in the opposite quadrant from *Y*-responses (a negative coefficient of regression), it means that, when oxidation reaction is carried out only with H$_2$O$_2$, it required a more time of reaction, but if Fenton reaction it is used (H$_2$O$_2$/FeSO$_4$)

it requires less time to achieve the same degree of modification. Based on these results, the sample of experiment N° 4 (50 wt% H$_2$O$_2$; 80ºC; 30 min and using Fenton reaction) was selected to continue with the characterization and will be hereinafter called oxidized rubber.
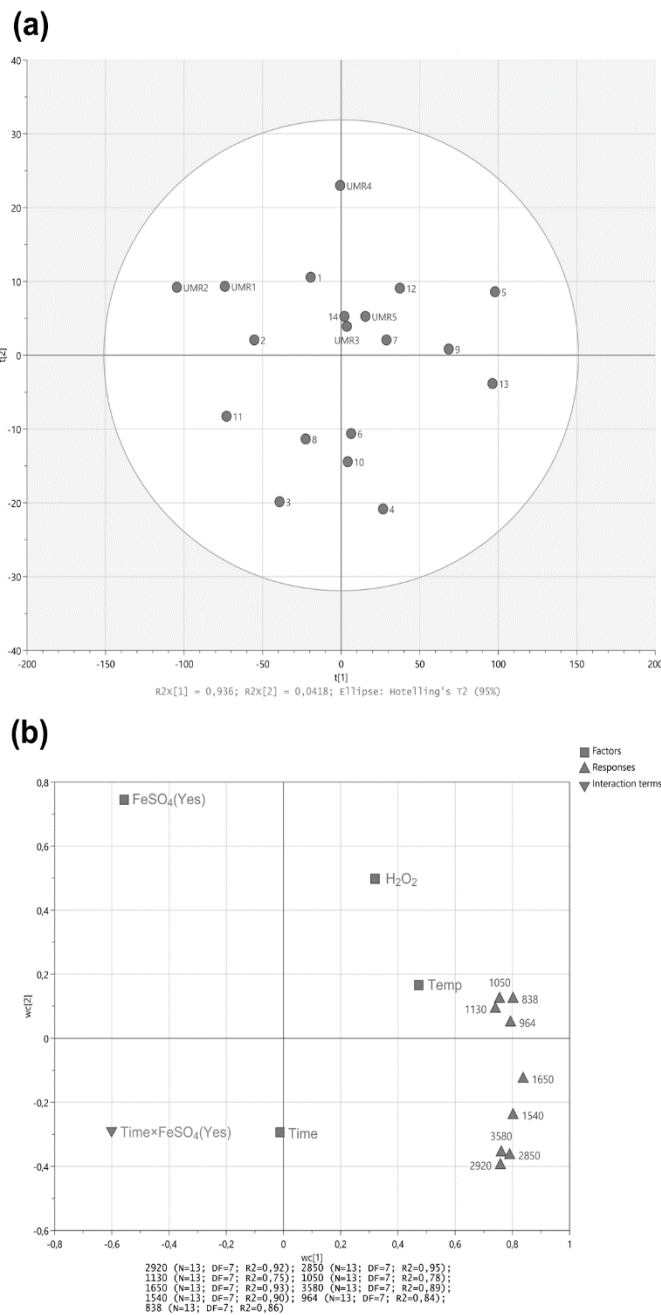
(a)

(b)

Figure 3. a) PCA scores plot t_1 vs t_2 ($p < 0.05$) of the 14 experiments plus five replicates of unmodified rubber (UMR). b) Loading scatter plot (w_1c_1 vs w_2c_2) of the PLS model obtained from the DoE.

A more detailed characterization of this oxidized rubber was performed. Figure 4 presents the FTIR-ATR spectra comparing the spectra of the unmodified rubber (UMR) with the oxidized rubber. The UMR spectra shows the characteristic bands of the rubber: 718 cm^{-1} CH deformation of 1,4-cis moiety, 962 cm^{-1} and 1530 cm^{-1} C–C stretching of aromatic ring, and CH stretching bands at 2850 cm^{-1} and 2915 cm^{-1}. The appearance of bands at 1050, 1100, 1130 cm^{-1} attributed to the C-O vibration of saturated primary alcohols are observed. At 1640 cm^{-1} a new signal appears attributed to carbonyl groups, while in the range of 3000-3500 cm^{-1} a broad band is observed attributed to the hydroxyl groups formed as a result of oxidation. These results confirm the oxidation of the rubber by the use of peroxides combined with Fenton.
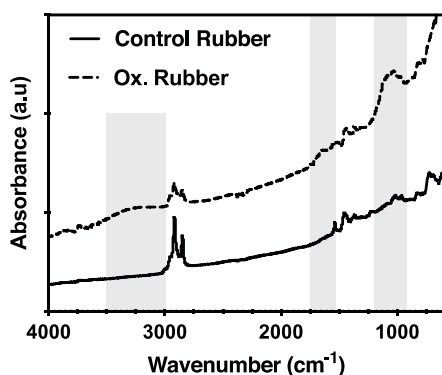
Figure 4. FTIR-ATR spectra of the oxidized rubber.

The rubber samples were analyzed by scanning electron microscopy and X-ray scattering spectroscopy to determine the change in the elemental composition of the surface before and after treatment. Figure 5a shows representative images of the oxidized and non-oxidized rubber. A change in the roughness of the rubber is observed after oxidation, while the control rubber has a rough surface, the oxidized rubber exhibits a more uniform surface. The concentration of representative elements such as C, O, S were determined to evidence chemical changes in the rubber's surface. Clearly, the increases of oxygen and carbon diminish concentration are ascribe to the oxidation process. In summary, all the results indicate a satisfactory surface modification of the rubber particles.
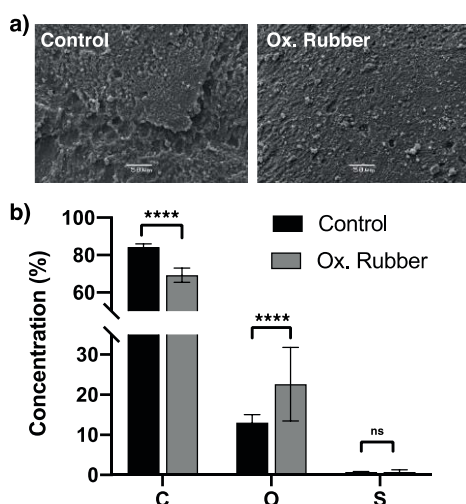

Figura 5. a) SEM images of unmodified and oxidized rubber, b) elemental at the surface of rubber particles ($n = 10$). (Error bars are standar deviation, **** $p<0.0001$, ns =not significant).

4. CONCLUSION

Rubber particles from end-of-life tires were oxidized by peroxide combined with Fenton method. Through infrared spectroscopy, it was shown that the method formed carbonyl and hydroxyl groups, and diminishes the bands related to double carbon bonds. The reaction conditions that showed the biggest modification in the infrared spectra of the rubber was determined through a Rechtschaffner Resolution V design, by analyzing PCA and the PLS interaction model obtained from it. The concentration of H_2O_2 and temperature of reaction are positively correlated with bands of C-O of alcohol in the spectra. A significant interaction Time×$FeSO_4$ indicates that if Fenton reaction it is used ($H_2O_2/FeSO_4$) it requires less time to achieve the same degree of modification than using H_2O_2 alone. The rubber particles that presented a greater differentiation in oxidation were studied in greater depth. The oxidized rubber particles shown to cause a decrease in the roughness of the surface of the particles. Through elemental analysis at the surface of rubber particles we demonstrated the increases of oxygen content attributed to the successful oxidation process. We envision peroxide and Fenton is a facile and scalable method to oxide rubber particles from waste tires for further use in application where hydrophilic compatibility is needed.

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