Compositional, thermal and morphological characterization of recycled and modified elastomers for inclusion in commercial cement mixtures

G K Mora-Rodríguez¹, C G Hernández Carrillo¹,², and Y Pineda-Triana¹
¹ Grupo de Integridad y Evaluación de Materiales, Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia
² Grupo de Investigación en Ingeniería Civil y Ambiental, Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia

E-mail: gina.mora@uptc.edu.co, carlosgabriel.hernandez@uptc.edu.co

Abstract. Elastomers are natural or synthetic polymers used in the automotive, mining, mold, assembly and other industries, due to their mechanical resistance in a wide temperature range from 60 ºC to 320 ºC; however, the waste generated is not disposed of properly, especially in the manufacture of tires, which generates environmental problems like inadequate final disposal, generation of toxic gases and public health problems; Therefore, in order to recycle these wastes, the present investigation modified elastomers superficially in order to produce strong adhesion with inorganic compounds like cement, through oxidation and sulfonation processes. For this purpose, NaOH and KMnO₄ solutions were prepared at a concentration of 5% and then impregnated in saturated NaHSO₃ solution. Subsequently, the modified elastomer was morphologically characterized by scanning electron microscope, thermogravimetrically by differential scanning calorimeter; compositionally by infrared spectroscopy, Raman spectroscopy, X-ray fluorescence, energy dispersive X-ray analysis and hydrophobic tests using contact angle techniques, in order to establish morphological and chemical compatibility with inorganic compounds. Results evidenced inclusion of functional groups OH, C = O and SO₃⁻, the reduction of carbon present in weak bonds and the presence of inorganic components such as potassium, sodium, manganese and sulfur were evident. The scanning electron microscope shows an increase in the roughness and contact surface of the elastomer as a function of the inclusion of polar functional groups by surface chemical treatment. These characteristics are to generate greater inclusion and compatibility of elastomers of an organic nature in inorganic compounds like cement matrices.

1. Introduction
Cement is the largest construction material used in the world [1]. In addition to being essential for infrastructure and building construction, cement is an essential industrial product for economic development; however, its production requires an industry with high energy consumption, generating a large amount of energy resources, greenhouse gas emissions and air pollutants generated in the production process [2,3]. As an alternative, industrial by-products have become a new field for the development of cement with inclusions of recycled materials; elastomers from discarded rubber tires are contaminating agents and a latent danger to health and their storage in deposits has generated great problems due to the gradual depletion of available sites for their disposal [4]. Therefore, the inclusion
of these in mixtures of cement contribute to the fight against the depletion of natural resources, the reduction of greenhouse gases and the elimination of solid waste [5-7], which have generated hardness and resistance to acid attacks and impact than ordinary concrete, thermal and acoustic insulation properties [8-10]. Nevertheless, rubber has poor interfacial compatibility with inorganic materials, since the cement paste is a hydrophilic material, while the surface of the crumb rubber is hydrophobic. Therefore, the adhesion between rubber and cement is poor, which damages the mechanical properties of the rubber cement matrix material and limits the development and application of rubber cement products [9]. However, by treating the surface through the inclusion of chemical surface modifying agents, it is possible to increase the roughness and polarity of the surface or the hydrophobicity of the rubber [9-11].

2. Materials and method
The rubber elastomer was obtained by mechanical separation of the recycled tire; after washing and dehydrating in oven at 60 °C for 24 h, after it is crushed and sieved, selecting the retained particulate material in sieves with meshes of 300 µm, 595 µm, and 841 µm. Subsequently, the rubber was impregnated NaOH solution of 5% concentration for 24 h and 240 h; then it’s washed in distilled water and dried in oven at 30 °C; previously, the treated rubber is added in a 5% solution of KMnO₄ together with sulfuric acid (H₂SO₄) as buffer solution (pH 2-3). The resulting rubber was rinsed in distilled water and impregnated in a saturated solution of sodium bisulfite (NaHSO₃) at 60 °C for 1 h to complete the rubber sulphonation reaction [9].

3. Results and discussion

3.1. Thermogravimetric and differential scanning calorimetry analysis
Figure 1 shows the results of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of rubbers during heating, from room temperature to 700 °C, which was carried out from room temperature to 700 °C, with a heating rate 10 °C/min.

![Figure 1. TGA and DSC analysis of rubber.](image-url)

The Figure 1 shows the initial phase the volatilization of oils and processing additives, or any other element with low molar mass and low boiling temperature till 200 °C, the weight loss reached 1.61% attributed to humidity. Subsequently, the greatest mass loss was in temperature range of 200 °C - 500 °C, due to the decomposition of the polymeric material, the release of organic vapours and the formation of waste similar to coal. Therefore, the thermogravimetric characterization corresponds to commercial rubber waste [12-14].
3.2. X-ray fluorescence characterization

To establish the variation of the chemical elemental composition of the rubber and the effect of the NaOH treatment at different exposure times, X-ray fluorescence (XRF) was used, through the PANalytical minipal2 pw4025 equipment; the results are shown in Table 1.

| Table 1. Elemental chemical composition (%) of elastomers treatments. |
|---------------------------------------------------------------|
| Rubber                  | Na  | Al | Si | P   | S    | K | Ca | Mn | Fe | Co | Cu | Zn |
| Reference              | -   | 13.0| 8.9| 0.6 | 20.1 | 0.2| 1.3| 0.7 | 4.9 | 0.5 | 0.5 | 47.3 |
| 24 h NaOH Impregnation  | 2.7 | 5.0 | 0.8 | 21.9 | 0.5 | 0.5 | 8.7 | 1.5 | 0.7 | 0.5 | 55.2 |
| 240 h NaOH Impregnation | 11.0| 2.6 | 4.8 | 0.6 | 18.6 | 0.46| 0.5 | 9.4 | 1.01| 0.6 | 0.5 | 47.6 |

Table 1 shows an increase in Mn element, from 0.66% to 9.40%, which indicates that the inclusion of the rubber in KMnO₄ solution served as oxidizing agent; similarly the inclusion of the Na element in the NaOH treatment is observed at 240 hours of immersion in the solution; therefore, it’s assumed that the NaOH hydrolyzes the acidic and/or carboxyl groups present on the tire rubber surface [15].

3.3. Characterization of the rubber surface by infrared spectroscopy

The Fourier Transform Infrared Spectroscopy (FT-IR) characterization was used to analyze the variation of the functional groups on surface of rubber after impregnation, using a Shimadzu FT-IR, IR Prestige-21, resolution of 2 cm⁻¹ and with configuration attenuated total reflectance (ATR). Figure 2 shows the spectra of the reference elastomer, treated at 24 hours and 240 hours with NaOH, group signal.

![Figure 2. FT-IR spectrum of reference rubber and treated chemically.](image)

The results evidence the characteristic signals of the elastomer with a magnitude of frequency around 2910 cm⁻¹ and 2846 cm⁻¹ of C-H bond [12]; signals of the vibratory in the range of 2960 cm⁻¹ – 2850 cm⁻¹ are associated with the CH₃ symmetric and asymmetric stretching vibrations of C-H bonds in CH₂ groups present in aliphatic elastomer chains and signals of the vibratory movement bending of the CH₃ around 1429 cm⁻¹ and CH₂ at 1371 cm⁻¹ [16]. Signs appear at 1371 cm⁻¹, characteristics of the hydroxyl functional group that starts at 3410 cm⁻¹ to 3201 cm⁻¹. About 1538 cm⁻¹, the carbonyl group signal and about 1080 cm⁻¹ apparently sulphonates.
3.4. Raman spectroscopy characterization

Raman spectroscopy is complementary to FT-IR and was used to analyze and corroborate the presence and variation of functional groups on the rubber surface after chemical treatment; for this purpose, a Thermo Scientific Smart Raman device was used. Figure 3 shows the results of Raman spectroscopy.

![Raman spectrum](image)

**Figure 3.** Raman spectrum of reference rubber and treated chemically.

Like FTIR, Raman spectroscopy shows an increase in intensity as the treatment time with NaOH increases, due to the inorganic processes reacted; additionally, it’s observed the symmetrical stretch of CH\(_2\) at 2850 cm\(^{-1}\). The deformation of CH\(_2\) on the 1452 cm\(^{-1}\), flexion of the CH at 1293 cm\(^{-1}\) and the \(\text{C=O}\) and \(\text{SO}_3\) at wavelengths less than 800 cm\(^{-1}\) one; however, noise is observed at low wavelengths due to the vibration mode of a large amount of small graphitic crystallites in the carbon atoms derived from the polycrystalline tire [17].

3.5. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

The morphological and elemental chemical composition evaluated in rubber is analyzed in Figure 4, obtained by scanning electron microscope (SEM) in Carl Zeiss EVO-MA10 equipment, previously coated with platinum using sputtering equipment Quorum Q150R-ES, to obtaining images with higher resolution.

![SEM images](image)

**Figure 4.** Scanning electron microscopy of rubber and treated chemically. (a) Reference rubber. (b) 24 h reaction with NaOH. (c) 240 h reaction with NaOH.
The SEM images of the rubber indicate a greater surface roughness as time increases with sodium hydroxide [18]; with 240 hours of NaOH treatment; therefore the treatment carried out increased surface area and consequently greater chemical activity. Additionally, the results of energy dispersive X-ray spectroscopy (EDS) are observed in the Table 2, in order to determining the carbon content variations and verify the compositional changes of the rubber product of the chemical treatment.

### Table 2. Elemental chemical composition measured by EDS in rubber and treatments.

| Rubber             | Elemental chemical composition (% Weight) |
|--------------------|------------------------------------------|
|                    | C  | Si | S  | Ca | Mn | Zn | Cl | K  |
| Reference          | 100.00 | -  | -  | -  | -  | -  | -  | -  |
| 24h NaOH impregnation | 95.60 | 0.46 | 0.79 | 0.05 | 1.05 | 2.03 | -  | -  |
| 240h NaOH impregnation | 95.18 | 0.69 | 0.89 | 0.15 | 1.37 | 2.03 | 0.05 | 0.04 |

Elemental chemical composition measured by EDS of the rubber and its treatments shows a small variation in the C content, attributed to the degradation of the weak carbon bonds by the chemical treatment. Likewise, the inclusion of inorganic elements from the solutions is observed; These compounds form a large amount of hydrogen bonds and ionic bonds between the rubber and the cement matrix, greatly improving the adhesive strength of the rubber in the cement matrix [9].

#### 3.6. A subsection contact angle analysis

The purpose of the sulfonated reaction of the rubber surface is to increase the polarity of the surface or the hydrophilicity of the rubber [9]; evaluated by the use of the high-resolution electric microscope LEYCA model dvm 2500. Figure 5 shows the images of the contact angle test before and after rubber modification.

The contact angles of the water with the reference elastomer, treated with NaOH at 24 h and 240 hours at 77°, 68°, and 61° respectively. The contact angle of the elastomer with the water decreases slightly with the chemical treatment, in addition there is a greater decrease with a reaction time of 240 hours; therefore, the sulfonation time of 1 h generates a sufficient reaction for a greater change in the contact angle between the rubber surface and the water [9].

![Figure 5. Contact angle between elastomer and water. (a) Reference rubber. (b) 24 hours of treatment. (c) 240 hours of treatment.](image)

### 4. Conclusions

Thanks to the set of compositional and morphological characterizations, it was possible to determine the variation in surface modification by oxidation and sulphonation of the rubber. These treatments introduced hydroxyl, carbonyl and sulfonate groups on the rubber surface, to improve the interfacial compatibility with inorganic materials such as cement; evidenced in the increase of roughness in the surface and reduction of the contact angle of the rubber with water. These surface modifications in rubber allow the potential inclusion in cement mixtures, which contributes to the reuse of contaminated waste, reduction in the use of raw materials and consequently contribute against the depletion of natural resources.
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