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# Effect of oxidation of end-of-life tire rubber as aggregate substitute in cement mortars

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ABSTRACT

In this paper the possible use of end-of-life tire rubber as a substitute for aggregate in cement mortars was explored. The aim of this paper was to investigate the effect of rubber surface modification by acidic treatment on the final properties of mortars. In fact, through treatment with sulfuric acid at moderate concentrations, a significant improvement in rubber wettability and interaction with cement has been observed. The compressive strength of mortars containing 15%w treated rubber as a replacement of natural aggregate is comparable to those of standard mortars. This suggests that surface modification of rubber plays a very important role in the possible integration of end-of-life tire rubber in mortar and concrete. The results presented in this paper confirm that recycling in mortar and concrete is a promising way for improving rubber waste management and sustainable innovation in the construction industry.

## 1. Introduction

The increasing amount of solid waste in landfills has prompted researchers worldwide to focus on finding sustainable waste management solutions that promote recycling and minimize environmental impact [1–5]. One waste material that has received significant attention is end-of-life rubber tires, which are voluminous and pose a challenge for disposal (with European consumption at more than 3 million tons per year) [6,7]. In recent years, many researchers have explored the potential of reusing end-of-life rubber from waste tires to replace the aggregate fraction in concrete. This approach offers economic and environmental sustainability benefits while improving functional properties [8–17]. By valorizing waste materials and turning them into resources through the principles of circular economy, significant progress can be made towards sustainable development [18]. The composition of tires and the generation of significant volumes of waste tires make them attractive for such reuse [6,7].

Rubber tires are predominantly composed of organic materials such as rubber/elastomers and carbon black (around 70 %), with a smaller amounts of inorganic components (about 17 %), textiles, and additives (about 13 %) [19]. Various methods exist for handling waste tires, including landfilling, thermal conversion through combustion for energy production, or re-processing for raw material recovery [8]. However, landfilling and burning tires can have negative environmental consequences, such as disease-carrying insect and rodent habitats during landfilling or the emission of pollutants during combustion, posing risks to human health [20,21]. To address these concerns, waste tires are preferably treated through milling to produce granulates, chips, powders, and textiles for utilization in advanced applications [8]. One appealing solution is the partial substitution of mineral aggregates (sand and gravel) in concrete with recycled tire crumb rubber. This approach leads to cement-based composite materials that may exhibit improved ductility, tenacity, impact resistance, and thermal/electrical/acoustic insulation capacities [22]. Additionally, the use of rubber in concrete provides a twofold environmental benefit by reducing tire disposal's environmental impact and minimizing the need for mineral aggregate excavation from quarries or rivers [23]. However, incorporating rubber into concrete can result in a significant reduction in mechanical. This is mainly attributed to the different mechanical response of rubber compared to mineral aggregates and, more importantly, to the poor interfacial adhesion between rubber and cement paste [24,25]. In fact, the interfacial adhesion between the inorganic cement paste and the organic elastomeric component remains a major concern, leading to a reduction in mechanical properties and limiting the effective utilization of rubber in concrete [26]. To overcome this issue, and enable the structural use of rubber concrete, it is crucial to select formulations that ensure adequate mechanical resistance and address interfacial adhesion concerns. Researchers have suggested various physicochemical

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treatments, such as surface roughening, immersion in NaOH or $H_2SO_4$ solutions, and the use of additives like pozzolana [9,23,27,28]. Moreover, fiber insertion was suggested to improve the mechanical properties of the cement-based composites [9,29]. In recent years, plasma-induced radiation treatments have gained interest for their ability to modify only the surface properties of materials without affecting the bulk characteristics [30,31]. Plasma treatments have successfully enhanced the surface wettability and interfacial adhesive response of rubber through the introduction of oxygen-containing functional groups or coatings via plasma-polymerization [32]. Previous studies have explored radiation-induced surface modification of tire rubber using atmospheric plasma, resulting in improved toughness and mechanical properties of mortar composites [33].

Overall, the utilization of recycled rubber in concrete presents opportunities for sustainable waste management and the development of novel construction materials with improved properties. In this paper the interfacial adhesion between rubber and cement was studied, its optimization being required to avoid strength loss in rubber concrete.

## 2. Materials

For this study, rubber powder derived from end-of-life tires, with a particle size ranging from 0 to 2 mm, was provided by TerniEnergia. Sulfuric acid ($H_2SO_4$) 98 % from Sigma-Aldrich was used for the surface oxidation of the rubber. In the preparation of mortar samples containing recycled rubber, a cement Buzzi-Unicem II/B-LL 42.5 R was employed. Standardized sand CEN EN 196-1 (bulk density 1.63 g/cm$^3$) was supplied by "Société Nouvelle du Littoral". The Dynamon additive (AD) and the Viscofluid superplasticizer (SP) were supplied by Mapei. The granulometric distribution of sand and rubber powder used is shown in Fig. 1.

## 3. Methods

For the morphological analysis of the treated rubber surface, a Zeiss Merlin FESEM was used. The variation in surface tension related to the increased wettability of the rubber was determined through contact angle measurements using water. A Bruker Tensor 27 Fourier Transform Infrared Spectrometer was employed to inquire the presence of the functional groups formed on the surface of the rubber. The mechanical results of the mortar samples were obtained using a Zwick-Roell Z050 equipped with a 50 kN load cell. The tests were performed at a fixed displacement rate of 0.1 mm/min. Mechanical tests were realized on at least six specimens per sample. Surface oxidation of the rubber was carried out by immersing the rubber powder in $H_2SO_4$ at 15 %, 50 % and 98 % volume concentrations for 15 min. At the end of the process, the rubber was recovered and rinsed with copious amounts of deionized water. Subsequently, characterizations were performed, including contact angle measurements, FT-IR and FESEM analyses. The contact angle was measured on a rubber plate treated in the same way as the ground powder used. The rubber of the plate is the same type as the ground one; the FT-IR spectra performed on the samples, not reported here for brevity, are overlapping and indicate that it is the same material. The mortar mixing and preparation followed the guidelines of UNI EN 196-1, with a water-to-cement weight ratio ($w/c$) equal to 0.5 with 0.5 % by weight of cement of Viscofluid and 1 % by weight of cement of superplasticizer, and an initial sand-to-cement weight ratio of 3. The paste was poured into cylindrical molds with a diameter of 20 mm and a height of 40 mm, and the samples were then cured first for 24 h at 20 °C in an environment with 100 % relative humidity and then for other 27 days at 20 °C immersed in tap water. The rubber treated at different acid concentrations was replaced at 15 % by volume of the aggregate. The mix design of the prepared samples is: 20 g of water, 40 g of cement, 0.4 g of SP and 0.2 g of AD. When rubber is used as replacement of sand the quantity of sand and rubber are respectively 102 g and 8 g.

## 4. Results and discussion

FT-IR measurements were performed to study the effect of the modification treatment onto the pristine rubber surface, as shown in Fig. 2.

The rubber spectrum presents two main signals at 2913 cm$^{-1}$ and 2846 cm$^{-1}$ (due to · $\nu_{asym}$ $CH_2$ and $\nu_{sym}CH_2$), and a band at 2950 cm$^{-1}$ (due to $\nu$ $CH_3$). The pristine rubber spectrum is characterized by a sharp intense signal at 1535 cm$^{-1}$ due to C-S bond [34] that vanishes after the acidic treatment. The band at 1427 cm$^{-1}$ is due to $\delta$ $CH_3$, and the band at 1375 cm$^{-1}$ is due to $\nu$ S=O, a band at 1360 cm$^{-1}$ due to methylene $\delta$ CH and a low intensity band at 1300 cm$^{-1}$ due to skeletal C-C vibrations. In the rubber treated with sulfuric acid there is an intense signal at around 1070 cm$^{-1}$ associated to O=S=O stretching [35]. These new chemical groups grafted onto the surface could promote better interfacial adhesion with cement matrixes.

The presence of oxygen-containing functional groups improves the wettability of rubber plate with water, as visible from Fig. 3.

Consequently, a better interaction with the cement paste should be expected. Table 1 shows the results of water contact angle measurements for rubber treated with different concentration of sulfuric acid. It is evident that wettability improves with treatment in 15 % $H_2SO_4$ and

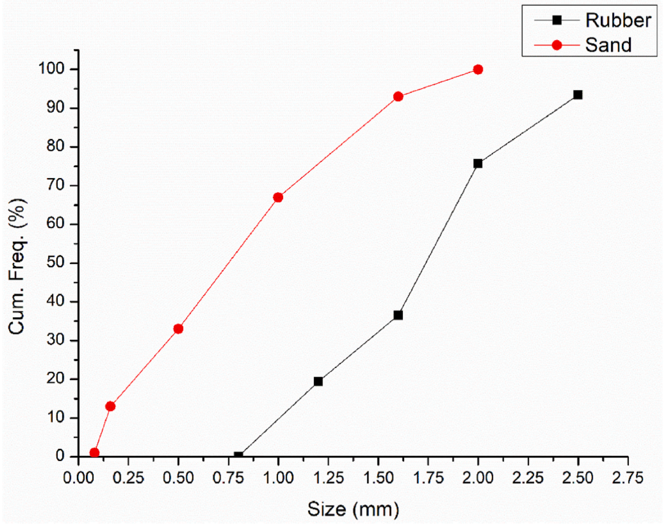

**Fig. 1.** Granulometric distribution of rubber powder and standard sand used.

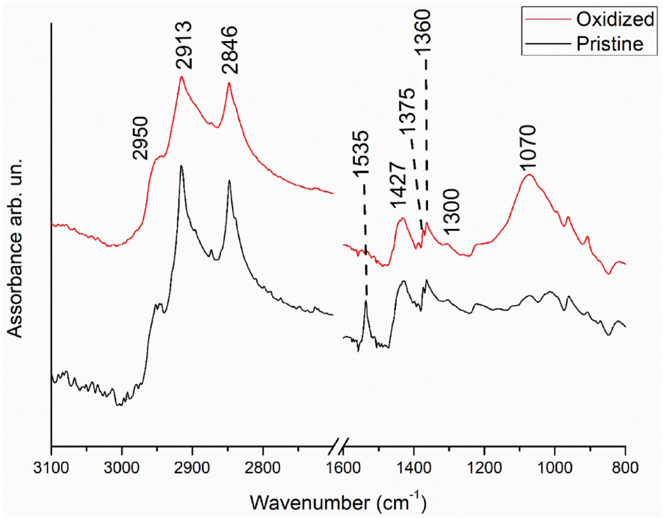

**Fig. 2.** FT-IR analysis of the pristine and oxidized rubber.

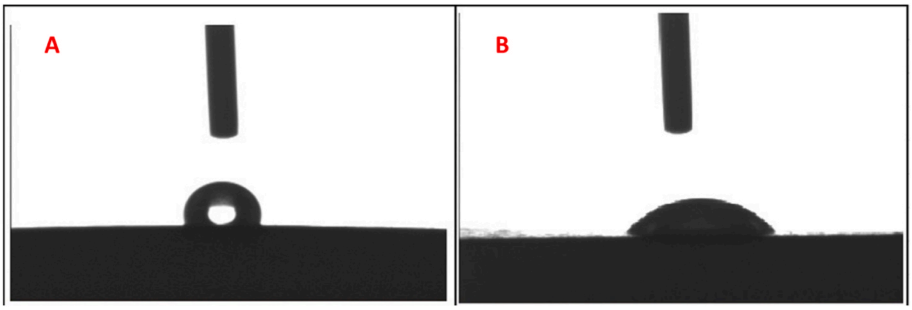

**Fig. 3.** Contact angle before acidic treatment (A) and after treatment for 15 min with 50%$_V$ solution of $H_2SO_4$ (B).

**Table 1**
Contact angle of rubber before acidic treatment (H0) and after treatment for 15 min with 15%$_V$, 50%$_V$ and 98%$_V$ solution of $H_2SO_4$ (H15, H50 and H98).

| Sample | Contact angle [deg] |
|---|---|
| H0 | 135 |
| H15 | 115 |
| H50 | 85 |
| H98 | 105 |

even more with treatment with 50 % $H_2SO_4$, while a too strong acid concentration reduces the wettability of the rubber.

It is interesting to compare these results with SEM observation. The roughness present on the surface of the rubber varies depending on the type of formulation used, the type of manufacturer, and the cutting and grinding methodology, as already known in literature [34]. From a morphological standpoint, the surface of the pristine rubber (Fig. 4 A) becomes smoother and less rough after the acid treatment, although some superficial micropores are already present, as indicated by the orange arrows reported in Fig. 4B. However, from the compression strength measurements it is evident that the effect of the surface chemical functionalization is more effective than the sheer rugosity. As shown in Fig. 5, the replacement of natural aggregate with rubber leads to a drastic reduction in the mechanical strength of the mortar. As already observed in literature, the use of waste material may result in mechanical properties loss. The granules of waste material act almost like pores, since they do not present a sufficient interaction with the cementitious paste [36]. Through functionalization, polar functional groups that can interact with the cement paste are created, and their effect can be directly related to the wettability. The mechanical tests results are perfectly in line with the contact angle values: the best-performing sample is the one with rubber functionalized with a 50%$_V$ $H_2SO_4$ solution. Functionalization at too high concentrations leads to the partial detachment of the functionalized layer from the rubber granule and, consequently, to lower mechanical properties [24]. Functionalization at too low concentration creates too few polar groups, so that the strength is only partially improved with respect to pristine rubber case.

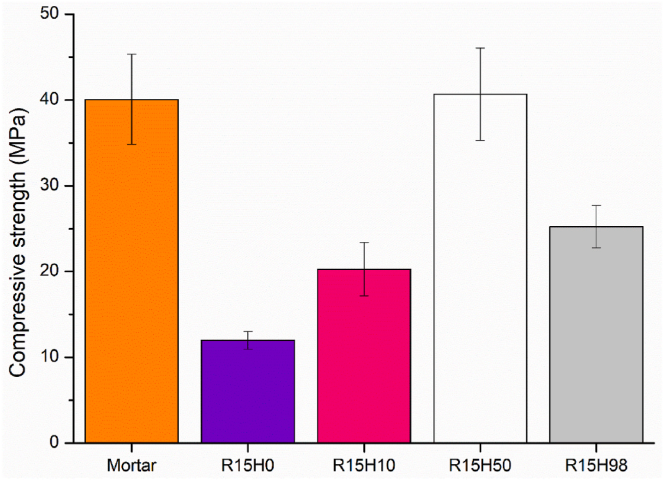

**Fig. 5.** Compression strength of mortar and mortar containing different percentage of treated rubber as replacement of aggregate.

## 5. Conclusions

The effect of the surface modification of rubber by acidic treatment on the final properties of mortars. was studied. The treatment with sulfuric acid led to a significant improvement in rubber wettability and interaction with cement. Provided that an acceptable functionalization technique is used, rubber can be inserted into mortar in appreciable quantity (15%$_V$), reducing its landfilled volume and allowing a lesser consumption of natural resources used as aggregate in these materials. This work demonstrates that a convenient rubber functionalization can be the key for using rubber powder without compromising the mechanical strength of mortar for example for sound insulation applications. In this way it is possible to recover the waste of rubber industries in a practical way.

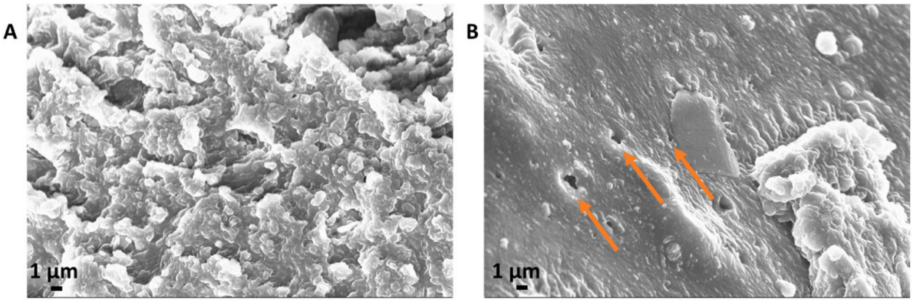

**Fig. 4.** FESEM images of pristine rubber (A), and of rubber after treatment with 50%$_V$ solution of $H_2SO_4$ for 15 min (B).

## CRediT authorship contribution statement

**Luca Lavagna:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Giovanna Colucci:** Data curation, Formal analysis, Visualization, Writing – review & editing. **Matteo Pavese:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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