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Alkali-Activated Mortars Modified by Epoxy-Carbon Fiber Composites Wastes

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Featured Application: Mortars formulated with different types of industrial wastes with improved mechanical properties can be obtained and used in civil engineering applications.

Abstract: Short chopped fibers coated by epoxy resin of different length (5 to 10 mm length) were added at low volume content (about 4.6% on the composite) to alkali-activated fly ash or metakaolin mortars. These uncured scraps derive from the production of carbon fiber-reinforced polymer composites and they are not presently recycled, despite their outstanding mechanical properties. The workability, microstructure, porosity, and physical and mechanical properties (mainly flexural strength) of the derived materials were investigated. Superior flexural strength and increased toughness were obtained. An acid treatment of the scraps further improved the mechanical properties of the mortars by changing the chemical structure of the surface, thus increasing the interaction with the inorganic phase. These results foster the use of these wastes to improve the performance of low carbon footprint building materials such as alkali-activated composites in the building industry.

Keywords: epoxy/carbon fibers composites; recycling; industrial wastes; alkali-activated mortars; mechanical properties; fly ashes

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1. Introduction

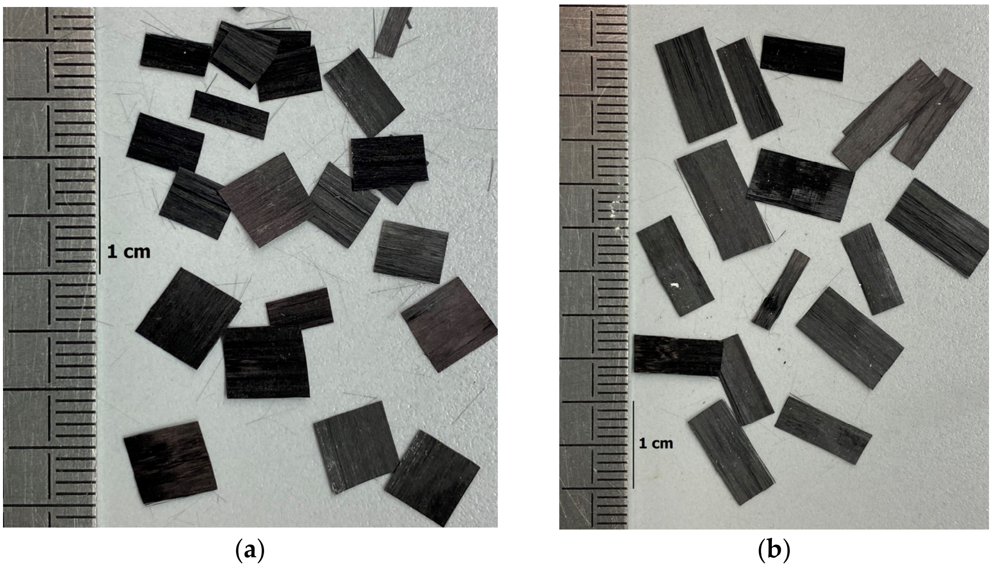
Epoxy resins reinforced by carbon fibers have outstanding mechanical properties and, because of their low density, high values of specific strength and modulus. As a result, they are applied in many sectors, such as the automotive, aeronautical, and nautical industries. Moreover, their demand is forecast to grow in the future [1,2]. A large quantity of scraps is generated during production and, at present, these scraps are discarded. The recovery of bare fibers is either energy consuming (pyrolysis of the matrix) [3,4] or involves the dissolution of the epoxy matrix through complex chemical reactions [5,6]. The direct reuse of the scraps has been proposed for other types of composites, such as in the formulation of alkali-activated mortars (AAMs). These promising materials [7,8] are used as binders as an alternative to traditional Portland cement, which has a significant carbon dioxide footprint [9]. Although characterized by a lower environmental impact, AAMs suffer from a number of drawbacks, such as extreme brittleness and low dimensional stability. The most frequently used solution to these problems is the addition of fibers. Polypropylene fibers [10], in addition to steel [11] or basalt [12] fibers, are commonly used for this task. The possible reuse of composite scraps [13] to obtain a similar improvement could provide a large environmental benefit. In this research, the effect of untreated scraps of different length on the properties of mortars formulated with metakaolin or fly ashes activated by alkaline solutions was investigated. The added amount of waste (about 4.6 vol% of the mortars) was derived from previous studies [13], which proved how this amount provided the best conditions to obtain good mechanical properties in similar materials. Moreover, a mild chemical pre-treatment of the scraps was performed to investigate a possible means to improve the fibers–matrix interactions. In this case, the aim of the chemical treatment was not to dissolve the epoxy resin surrounding the fibers, but only to modify the outer surface of the epoxy layer.

2. Materials and Methods

2.1. Composites Waste Scraps

Pre-preg off-cuts derived from the production of carbon fiber/epoxy composites (CF/EP), hereafter defined as waste scraps (WS), were kindly supplied by REGLASS (Minerbio, BO, Italy). The as-received scraps had an almost rectangular shape with side dimensions ranging from 10 to 40 cm. They were made of multiple CF/EP impregnated layers with an average thickness of 300 ± 20 μm. The density of WS is 1.55 ± 0.05 g/cm^3.

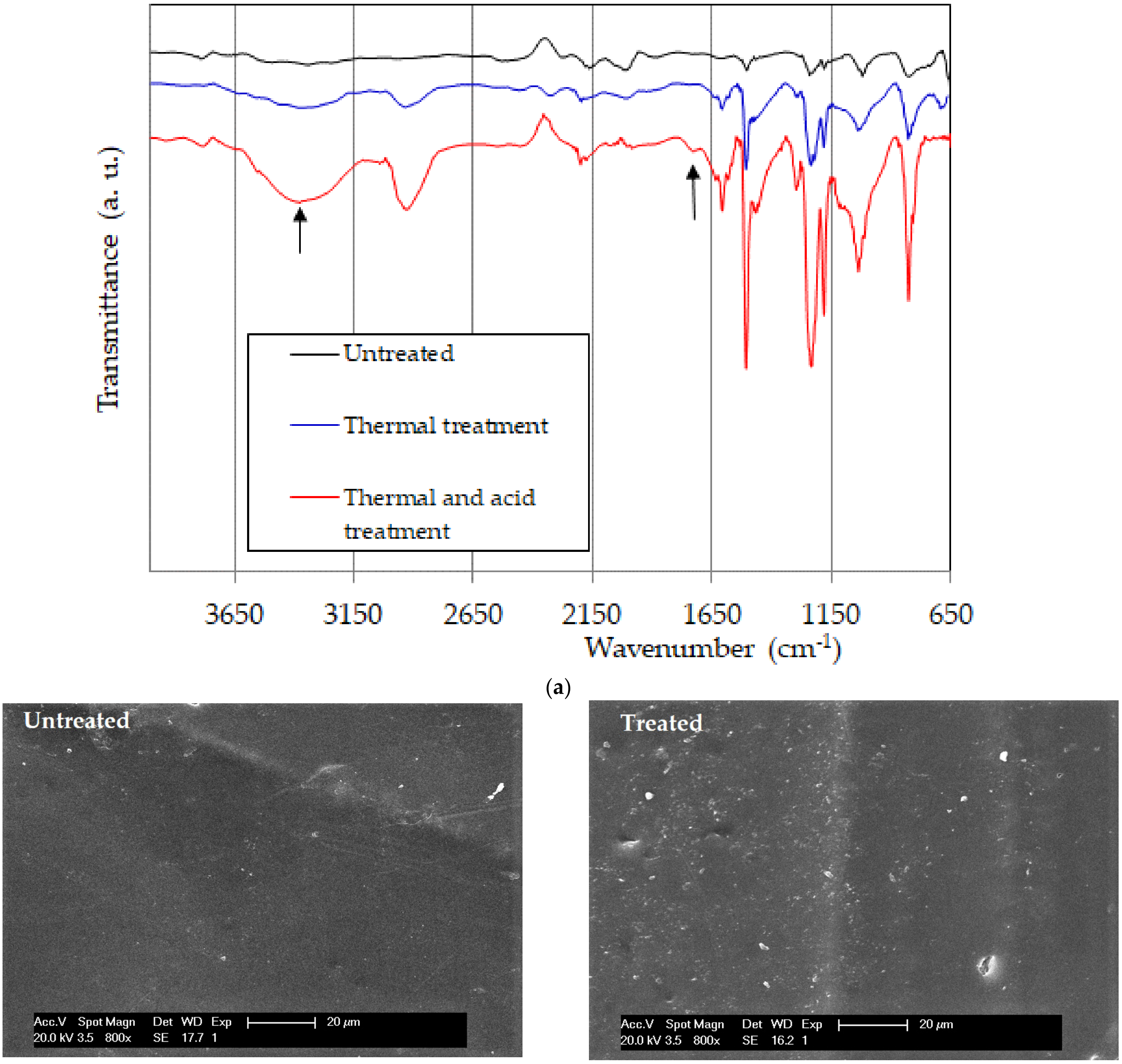
The original multiple layer sheets were treated for 1 h at 130 °C to complete the cross-linking reactions and then shredded to obtain fibers bundles with the length of either 5 ± 1 mm or 10 ± 1 mm, and lateral size ranging from 3 to 6 mm (Figure 1).



(**a**) (**b**)

Figure 1. Chopped bundles of WS with 5 (**a**) and 10 (**b**) mm length.

Some chopped bundles of both lengths were immersed in a sulfuric acid solution (0.2 M) for 1 h. The treated surfaces were submitted to ATR IR analysis over the wavenumber range of 650–4000 cm^{-1} using a PerkinElmer Spectrum One FT-IR spectrometer equipped with a Universal ATR sampling accessory. A total of 32 scans were taken for each spectrum at a resolution of 2 cm^{-1}. Figure 2a shows the infrared spectra of the treated and untreated composites. As can be seen, the thermal treatment promotes the full curing of the epoxy resin. The ring opening reaction creates some –OH groups as evidenced by appearance of a weak band centered at 3350 cm^{-1}. In the treated samples, the same band becomes more intense and a small band appears at 1730 cm^{-1}. This band is probably related to the presence of carbonyl groups derived from the partial resin degradation. These results agree with those reported in the literature [14,15]. In addition, SEM micrographs (Figure 2b) of the samples (FEI, XL20 Scanning Electron Microscope), obtained after gold metallization, highlighted that the treatment affects only the surface of the scraps.



(**a**)

(**b**)

Figure 2. (**a**) FT-IR spectra of the treated and untreated fiber bundles. (**b**) SEM micrographs of the untreated and treated scraps.

2.2. Activators

Sodium hydroxide (NaOH) reagent grade (Carlo Erba, Milano, Italy) and sodium silicate (Na_2SiO_3) solution (Ingessil, Verona, Italy), a viscous liquid produced for the cement industry with a water content of 57 wt% and a SiO_2/Na_2O ratio of 3, were used as alkaline activators.

2.3. Binders

Fly ashes (Type F) were derived from the plant of Torrevaldaliga (Roma, Italy) and had the following chemical composition: SiO_2 49.37%, Al_2O_3 29.63%, 0.05 Na_2O%, K_2O 0.06%, CaO 6.63%, MgO 1.05%, Fe_2O_3 2.71%, SO_3 0.33%, loss on ignition 3.28%. The average dimension (D_{50}) was 22 µm.

Metakaolin was obtained by calcining commercial kaolin (Argirec B24, AGS Mineraux, Clerac, France) at 700 °C for 5 h. The D_{50} was 40 μm.

2.4. Aggregate

Normalized silica sand conforming to the EN 196-1 Standard was used as fine aggregate (max diameter 0.7 mm).

2.5. Mixing Procedures and Compositions

A Hobart machine conforming to the EN 196-1 Standard was used. Sodium hydroxide 8M solution and sodium silicate were dosed according to the quantities determined in previous experiments [13,16] according to the different binders. The aim of the added quantities was to maintain an appropriate Si/Al and Na/Al ratio. The activators were first mixed together and cooled to room temperature. Subsequently, binder, sand, and water were added. The mixing procedure lasted 7 min. Eventually, the scraps were added and the fresh mortars were mixed for an addition 2 minutes. Table 1 shows the composition of all the investigated mortars and their labels. It should be highlighted that the reported results refer to this mixing procedure. Different mixing conditions may lead to different microstructures and consequently different results. Mortar workability was reduced by the addition of waste to a maximum of 10% in the case of 10 mm bundles and 4% for 5 mm bundles. However, these reductions allowed the efficient filling of the molds without the formation of any macroscopic defects. By comparison, longer fibers (15 mm) altered the rheological behavior of the mortars, thus implying the necessity to introduce either a superplasticizer additive or an additional quantity of water. The present study was thus limited to this maximum length to ensure other mix-design parameters were not altered. From the fresh mortars, specimens of 25 × 25 × 100 mm were cast in silicone molds and kept in polyethylene bags at 23 ± 2 °C for 24 h. After demolding, they were stored at 23 ± 2 °C and 70 ± 5% R.H. until the scheduled test times. The same fresh mortars were used to cast the specimens for pull-out tests (see next paragraph).

Table 1. Mortar composition (g) and labels.

Sample	Metakaolin	Fly Ash	Na_2SiO_3	NaOH	Water	Sand	WS
M 0	100	0	30	30	10	100	0
M 5 [1]	100	0	30	30	10	100	10
M 10 [1]	100	0	30	30	10	100	10
F 0	0	100	38	8	7	100	0
F 5 [1]	0	100	38	8	7	100	9
F 10 [1]	0	100	38	8	7	100	9

[1] Mortars containing treated waste of 5 and 10 mm are labelled as M 5_T, M 10_T, F 5_T, and F 10_T.

The volume fraction of waste scraps (WS) in all of the investigated mortars was about 4.6 vol% of the composite amount.

2.6. Tests

2.6.1. Water Absorption

The amount of absorbed water at room temperature and atmospheric pressure was determined following the EN 772-21 Standard on samples of 25 × 25 × 50 mm at 28 days of curing.

2.6.2. Mechanical Characterization

Flexural strength (three point bending test) and compressive strength were determined at 25 ± 2 °C and 60 ± 5% R.H. using a 100 kN testing machine (Wolpert-Amsler) after 28 days of curing. A testing rate of 10 mm/min was used. At least 5 samples were tested in flexural mode, 10 samples in compression mode.

2.6.3. Pull-Out Test

To evaluate the adhesion/interaction between the waste composite surfaces and the matrix, a modified pull-out test was performed. Waste composite sheets (40 × 150 × 0.3 mm) were partially embedded in the alkali-activated mortar (Figure 3). After 28 days of curing in the same conditions as those previously described, the loose extremity of the sheet was clamped to the mobile head of the testing machine while the mortar was clamped to the second plate. The maximum tensile shear stress required to pull out the embedded fraction of the composite sheet from the mortar was determined. A rate of 1.0 mm/min was applied in the test.

Figure 3. Specimens for the pull-out test.

3. Results

Figure 4 shows the water absorption for all of the investigated samples. The waste addition tends to reduce the amount of absorbed water. The effect is larger in fly ash materials than in metakaolin materials (about 10% maximum for metakaolin and 19% maximum for fly ash), due to the different characteristics of the precursors. No remarkable differences were detected for the different waste length, or for the treated and untreated wastes.

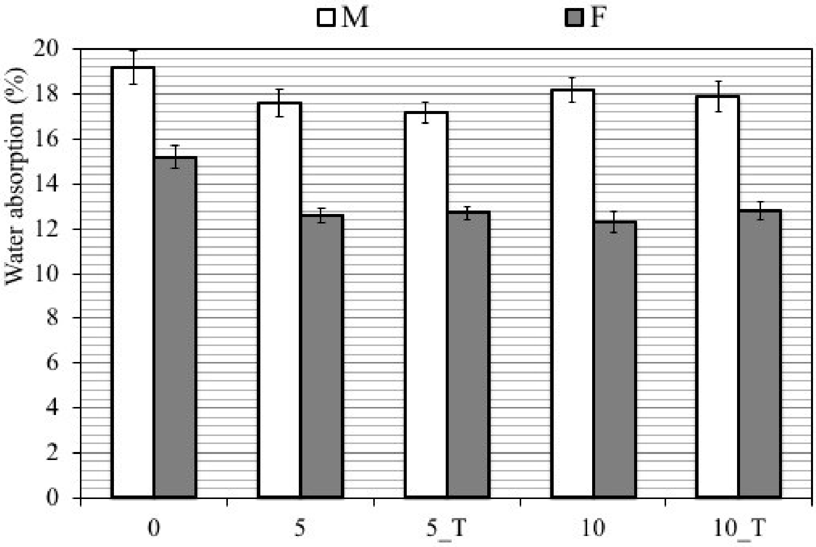


Figure 4. Water absorption of the investigated materials.

These results show that waste addition, at least at this amount, does not create porosities in the composites, either as air entrained or due to the imperfect adhesion between the matrix and the waste, i.e., from the creation of a porous interphase transition zone. The slight decrease can be ascribed to the substitution of a porous fraction (the matrix) with a nonporous one, the waste. The almost unchanged values of the treated fibers vs. the untreated fibers may imply good interaction of the unmodified epoxy resin surrounding the fibers with the ceramic matrix, as found in other research [17–19].

Figure 5 shows the flexural strength of the investigated composites. A progressive increase in the strength of the mortars takes place after adding the waste. Both the length value (from 5 to 10 mm) and the surface modification of the waste increase this mechanical property.

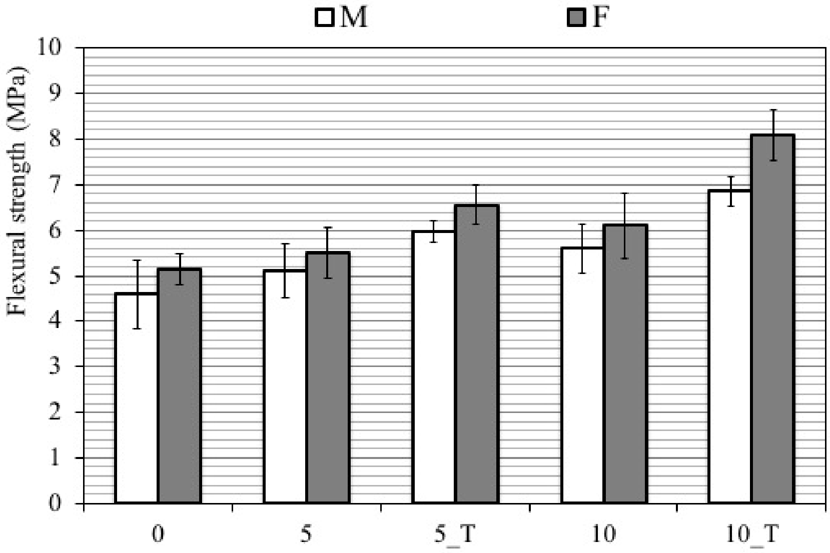


Figure 5. Flexural strength of the investigated materials.

Figures 6 and 7 report the plot of the load/mid span deflection results for the fly ash and metakaolin samples respectively.

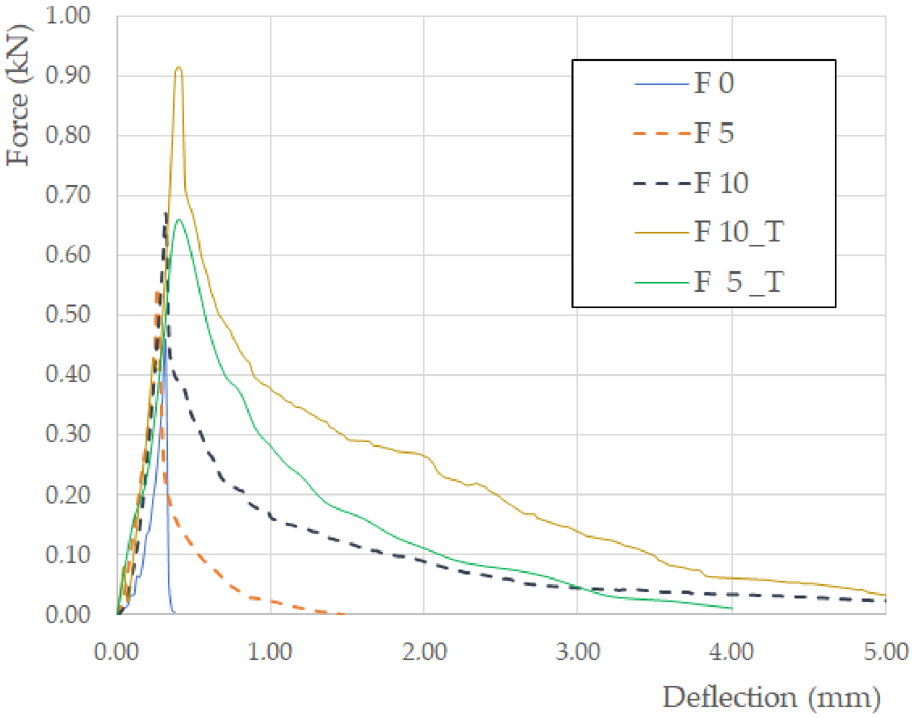


Figure 6. Load deflection plots for F materials.

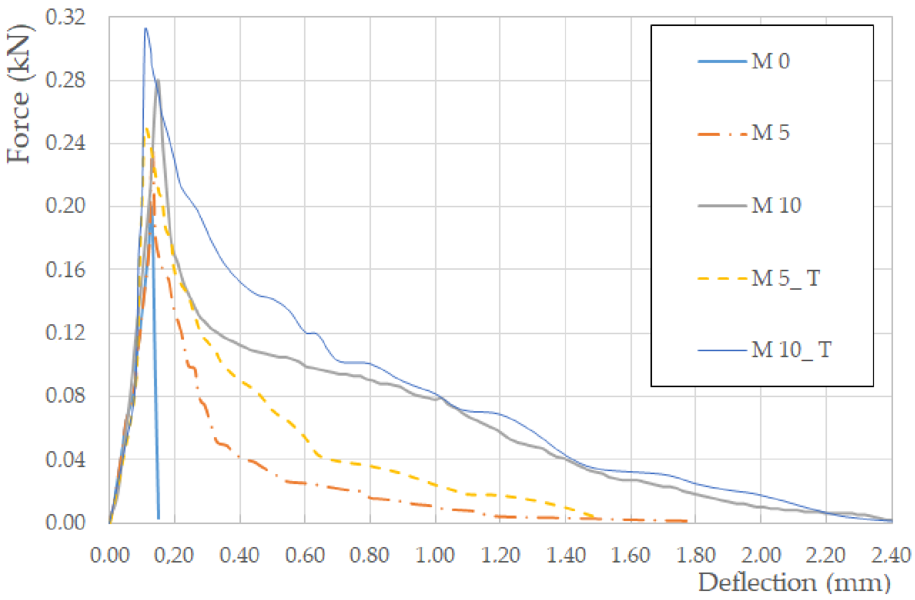


Figure 7. Load deflection plot for M materials.

Compared to the completely brittle, catastrophic behavior of the unmodified mortars, a toughening effect appears in the modified mortars. The bending behavior of the modified mortars can be defined as a deflection-softening effect. This effect increases as the length of the waste bundles increases or when the acid treatment of the scraps is carried out. The trend is thus consistent with that observed for flexural strength values (Figure 5).

Regarding the compressive strength of the mortars, no significant changes were found (Figure 8) in all of the modified mortars compared to the unmodified mortars.

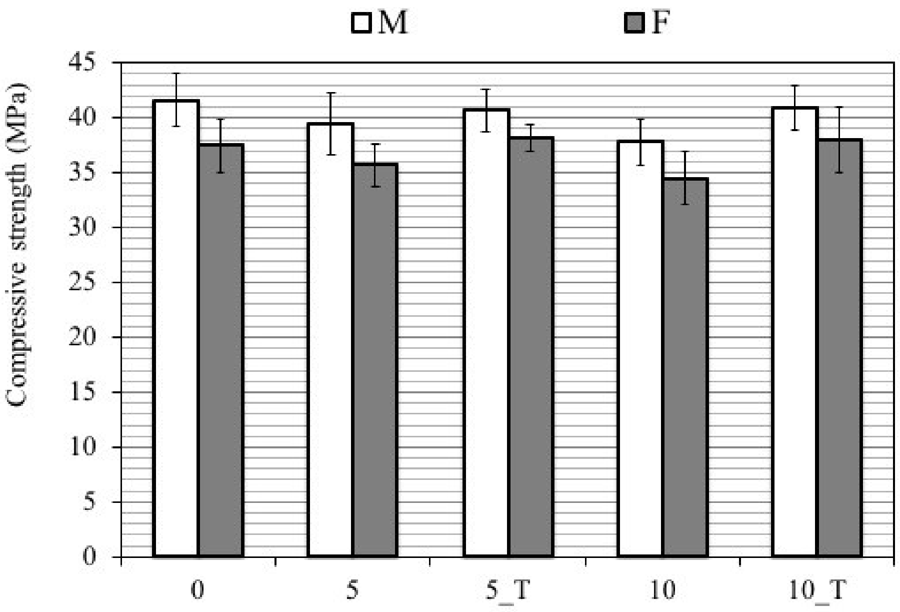


Figure 8. Compression strength of the investigated materials.

The reduction in porosity previously observed (Figure 4) derived from the presence of the nonporous volume of the scraps (4.6 vol%) is insufficient to change the mechanical response of the composite, i.e., the porosity of the 3D geopolymerized network is unchanged, and the prevailing, continuous matrix still governs the compressive properties.

In Figure 9, the results of the pull-out tests are shown. In both matrices, the shear stress required to pull out the waste composite increases. This effect is due to different contributions, as discussed below.

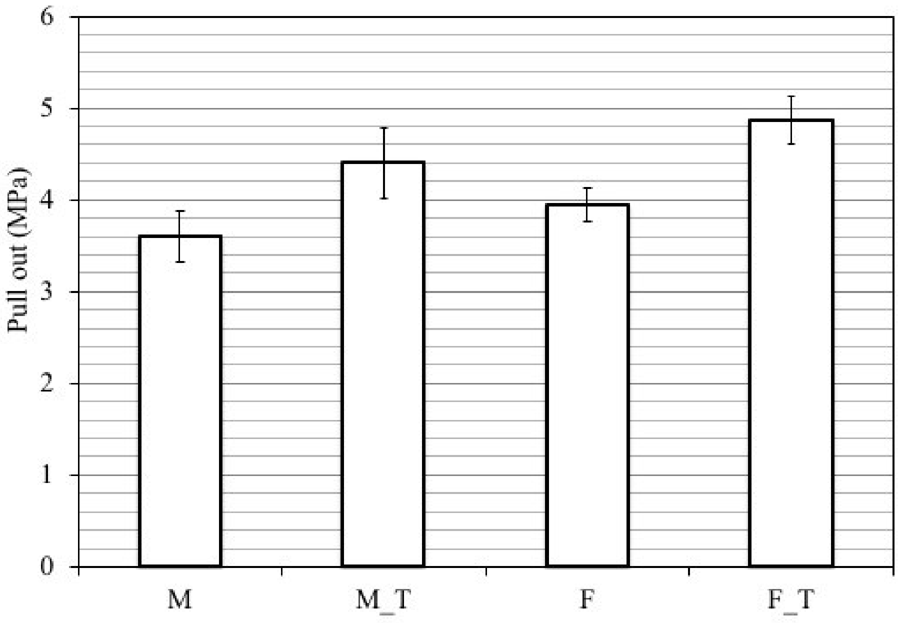


Figure 9. Pull-out test results.

4. Discussion

The direct use in mortars of waste carbon fibers that are embedded in the epoxy matrix allows the elimination of onerous pretreatments that would increase the economic and environmental costs of the process. Moreover, a reliable and complete removal of the polymeric matrix through those methods is difficult to obtain, thus creating an uneven surface in the reinforcement. Treatments may also damage the fibers, reducing their mechanical properties. Consequently, the use of recycled fibers in building materials may be compromised [20]. The good interaction of the epoxy resin with the alkali activated phase enables the homogeneous dispersion of the waste, up to the amount investigated here, without compromising the workability of the new composites. Both effects are supported by the reduction in the overall porosity of the mortars, which suggests increased durability of the same materials, a feature that will be further investigated in future experiments. By comparison, negative effects on the porosity were found by adding waste carbon fiber epoxy composites with micrometric dimensions [21]. From a mechanical perspective, the presence of the fibers increases the flexural strength of the mortars and inhibits brittle fracturing. Following the first crack in the matrix, the fiber bridging and pull-out effects enable energy dissipation. As found elsewhere, in either cement Portland composites [22,23] or in metakaolin geopolymers [24], the increased length of the fibers increases the flexural strength and ductility of the materials. The observed effect is higher than that found previously in Portland cement mortars [25]. The proposed acid treatment affects only the surrounding matrix and the fibers remain undamaged. However, it increases the density of permanent dipoles on the external surface of the epoxy layers, and the concentration of hydroxyl functional groups, as evidenced by FT-IR analysis. These functional groups can interact with the hydroxyl groups in the alkali-activated network, creating a stronger link between the two phases through hydrogen bonds. This last reaction may provide the greatest contribution to the enhanced adhesion; however, it should be noted that, in similar systems [26], the creation of Si-O-C strong covalent bonds was detected. A last possible contribution may result from the different smoothness of the pristine and treated epoxy surface. The chemical treatment may create a rougher surface, providing a higher mechanical interlocking with the geopolymeric matrix. This final possible contribution deserves deeper investigation. The effect of the different transition zone on the pull-out behavior of fibers in geopolymer has been previously determined [27]. The effect of surface treatments on recycled CF/EP has been discussed in previous research, however, a traditional Portland cement matrix was used. Thus, the aims were different from those of this research, in which alkaline solutions were used [20] to eliminate the residual of the epoxy matrix on the fibers, whose presence was considered to be detrimental, to increase the adhesion between the carbon fibers and the cementitious matrix. This treatment increased the tensile strength of the composites but no improvements in the compressive strength were obtained, and the proposed conditions could damage the fibers during a long contact time. In the case proposed in this paper, the etching treatment simply increases the interaction between the matrix and the reinforcement.

5. Conclusions

This research proved that is possible to reinforce alkali-activated mortars by simply adding untreated scraps of cross-linked carbon fiber/epoxy resin composite, thus increasing both the flexural strength and the toughness of the obtained materials. The good interaction between the epoxy and the ceramic matrix allows a uniform dispersion of the second phase. A mild etching treatment of the scraps, which is capable of increasing the interaction between the matrix and the reinforcement, was proposed. Although using this treatment will increase the environmental and economic impact of the process, a further increase in the mechanical properties can be obtained. The simultaneous recycling of different industrial wastes can lower the overall impact of building materials.

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