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# Bi-Layered Porous/Cork-Containing Waste-Based Inorganic Polymer Composites: Innovative Material towards Green Buildings

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**Abstract:** Reduction of the energy consumption and $CO_2$ emissions by the building sector might be a huge driver to mitigate climate change. One promising approach to mitigate energy consumption is the use of lightweight and low thermal-conductivity materials that could reduce the energy losses inside buildings and at the same time the use of heating and cooling devices that generate associated $CO_2$ emissions. In this study, different strategies to produce lightweight and low thermal conductivity inorganic polymers were evaluated and compared, including the first ever production of bi-layered porous/cork-containing waste-based inorganic polymer composites. The bi-layered composites showed the lowest density (461 kg/m$^3$) and thermal conductivity (94.9 mW/m K) values and reasonable compressive strength (0.93 MPa) demonstrating their interesting potential for enhancing the energy efficiency of buildings. Moreover, these composites were produced at room temperature, using an industrial waste (biomass fly ash) as precursor and a highly sustainable and renewable resource as light aggregate (cork), preventing the depletion of natural resources and the use of fossil-fuel derivates, respectively.

**Keywords:** industrial waste; recycling; thermal conductivity; natural aggregate; composite; alkali activation

## 1. Introduction

Despite the global effort attempting to reverse the impacts associated with climate change a recent study by the United Nations shows that causes and impacts of such action are accelerating rather than slowing down [1]. The greenhouse gas emissions, in which carbon dioxide plays a key role, have increased nearly 20% in the last 5 years (2015–2019) compared with the period 2011–2015. The $CO_2$ emissions from the combustion of fossils fuels and those arising from cement production hugely contribute to the growth of the anthropogenic carbon. The persistence of existing strategies will have devastating consequences for the environment, and therefore urgent actions to tackle climate change are imperative.

The building sector might play a vital role in climate change mitigation since it is responsible for a large share of the energy consumption (~40%) and $CO_2$ emissions (36%) in the European Union (EU) [2]. The energy efficiency of buildings deserves special attention considering that 75% of the EU buildings stock is energy inefficient [3]. To enhance the energy efficiency and decarbonize the building stock, new high-performance materials must be developed and used in building construction/rehabilitation. The use of lightweight concrete with low thermal conductivity is a promising approach to mitigate the energy losses inside buildings [4,5]. Portland cement has been the most widely used ingredient in mortars and concretes over the past century. However, concerns regarding the $CO_2$ emissions associated with its production [6] have led to the pursuit of alternative binders. Inorganic polymers emerge as the most promising avenue having much lower embodied $CO_2$, provided that proper mixture design is employed [7,8], and due to the possibility of using wastes as raw materials instead of commercial precursors [9] which further decreases the carbon footprint of these materials and alleviates the pressure exerted by the unprecedented volume of waste production estimated to reach a stunning 3.4 Bt in 2050 [10].

The feasibility of using lightweight inorganic polymers in low thermal-conductivity applications has been recently highlighted in review papers [5,11]. Amongst the various synthesis protocols that might be employed to produce lightweight inorganic polymers, the chemical foaming technique [12,13] and the use of lightweight aggregates [14,15] are the most common routes. In the former a porous body is produced due to the decomposition of the foaming agent in the alkaline medium releasing gas bubbles which are then trapped in the paste, while in the latter a reduction of density depending on the nature and amount of the aggregate is seen in the specimens. The use of natural and sustainable lightweight aggregates instead of fossil fuel-derived ones is a particularly attractive way to enhance the global sustainability of the construction sector [16,17]. Nevertheless, this possibility has hardly been considered and most of the studies used polymeric-based aggregates (e.g., polystyrene) [18,19] made from fossil fuels which deviates from the sustainability paradigm envisioned for the construction of green buildings. Nonetheless, it should be highlighted that some studies have used polymer wastes as light aggregates (e.g., polyurethane wastes [20], crumb rubber from recycled tires [21]) partially diluting sustainability concerns. In any case, the use of natural and renewable aggregates is expected to provide environmental benefits over synthetic or non-renewable materials.

Cork is a highly sustainable and natural material with a unique array of properties that set it apart from other materials. The sustainability of cork derives from the non-destructive harvesting from the oak tree (i.e., the bark is simply stripped from the tree) which has a lifespan of more than 200 years, and to the increase in the $CO_2$ uptake by the tree in the regeneration of a new cork layer. In addition, cork is very light and presents remarkable thermal and acoustic properties making it a truly multifunctional material [22,23], and a promising candidate as a light aggregate in the production of low-carbon building materials. Despite this, its use as light aggregate to produce inorganic polymer composites remained unexplored until the recent pioneering work by the authors [24,25]. Our initial work evaluated the feasibility of adding expanded black cork granules to metakaolin-based inorganic polymer matrices to produce ultra-lightweight composites [24]. Then, we studied the acoustic and moisture buffer properties of cork-containing inorganic polymer composites and demonstrated that the addition of black cork granules greatly enhances the specimens' sound absorption coefficient and grants the composite a reasonable ability to exchange water with the surroundings upon daily cycling humidity fluctuation [25]. Despite the promising results demonstrating the interesting potential of cork as a multifunctional lightweight aggregate to produce inorganic polymer composites, the specimens' mechanical performance was poor possibly due to the use of black expanded cork (thermally decomposed) rather than untreated cork. In addition, in those studies the composites were produced using only cork.

In this study, different strategies to produce lightweight and low thermal conductivity inorganic polymers were evaluated and compared, including the first ever production of bi-layered porous/cork-containing composites. The bi-layer inorganic polymer composite coupling load bearing capacity with thermal insulation properties might reduce the thermal bridges observed when using different construction layers and as a result decrease the energy losses inside buildings, and this further demonstrates the innovation of the present study. The influence of using a foaming agent, cork, or their combination in the specimens' thermal conductivity and mechanical performance was evaluated. This investigation is a significant step forward in comparison with other literature studies attempting to clarify the most promising synthesis protocol to produce materials combining low thermal conductivity and moderate load-bearing capacity. In addition, this innovative material was produced using substantial amounts of an industrial waste (biomass fly ash) in the binder composition, in line with the circular economy concept. Biomass ash is a problematic waste generated in very high amounts in power plants due to the growing interest in the renewable energy production [26]. Worldwide production of this ash (including bottom and fly ashes) reach 500 Mt/year, mostly disposed in landfills [27]. In this study, biomass fly ash was used as the main source of reactive silica and alumina to produce a high added-value building material. The use of unexplored industrial wastes to produce innovative products for the construction sector is a very important strategy for achieving sustainable development.

## 2. Materials and Methods

### 2.1. Materials

Cork granules, size comprehended between 0.5 and 2 mm and 64 kg/m$^3$ apparent density, were used as light aggregates. The cork granules were kindly supplied by a Portuguese cork industry (Relvas II-Rolhas de Champanhe S.A. Mozelos, Portugal).

Biomass fly ash waste produced by a Portuguese pulp and paper plant was used as the prime silica and alumina source to produce the inorganic polymers, while smaller amount of metakaolin (Argical™ M1200S, Univar®) was added to the compositions to adjust the $SiO_2/Al_2O_3$ ratio. The chemical activation of the fly ash/metakaolin blends was performed using a mixture of sodium silicate ($SiO_2/Na_2O$ = 3.2; Quimiamel, Portugal) and 10 M sodium hydroxide (ACS reagent, 97%; Sigma Aldrich, Algés, Portugal), consisting of 3 parts of sodium silicate and 1 part of sodium hydroxide solution (in weight).

Aluminium powder (Expandit BE 1101, Grimm Metallpulver GmbH, Roth, Germany) was used as foaming agent, while an anionic surfactant (Hotaspur OSB, Clariant, Porto Portugal) was employed to stabilize the gas bubbles.

### 2.2. Inorganic Polymer Synthesis

In this study three different sets of samples were produced: (i) foams: by adding varying amounts of Al powder to the inorganic polymer slurries; (ii) cork foams: adding 75 vol.% of cork and variable amounts of Al powder; and (iii) bi-layered composites formed by a porous upper layer with variable porosity, and a bottom layer containing cork (75 vol.%). Additionally, a dense composition (prepared without using Al or cork) was prepared and used as reference. This is further described in the schematic drawing shown in Figure 1.

The mixture design of the reference composition was selected following previous works by the authors [25,28]. Briefly it involves mixing the fly ash/metakaolin blend (70:30 wt.%) inside a plastic bag for 1 min, and then the alkaline solution (prepared 24 h in advance due to its exothermic nature) is added to the solid precursors in a 1:1 weight ratio and vigorously mixed using an intensive mixer (KichenAid®, having a geometry in accordance with DIN 1164, coupled with a flat paddle) for 10 min to synthesize the inorganic polymer. The production of the foams required an additional step in which the foaming agent (amount depending on the composition but ranging from 0.05 to 0.10 wt.%) and the surfactant (0.05 wt.%) were added to the paste and mixed during 2 min. In the case of the cork foam production, the last step also involves the addition of cork granules (75 vol.%) to the foamed slurry and their mixture for 1 min.

The synthesis of the bi-layered composites is a two-stage process: in the first the foamed cork-containing slurry (prepared as in cork foams) is casted into metallic molds (4 × 4 × 16 cm$^3$) filling half of its volume (i.e., 2 cm thickness × 4 cm width × 16 cm length); and then a second paste (foamed slurry prepared as in foams) is applied over the partially cured first layer. The samples were sealed with a plastic film to avoid dehydration upon curing and cured for 24 h at room temperature (23 ± 2 °C), after which they were demolded and cured at ambient temperature and humidity till the 28th day.

The amount of cork added to the compositions was kept constant (75 vol.%) since this investigation intends to act as a proof-of-concept demonstrating the possibility of using bi-layered porous/cork-containing waste-based inorganic polymer composites as an innovative and energy saving building material. Nevertheless, higher amounts might be employed to enhance the specimen's thermal and acoustic properties, and this will be evaluated in future work.

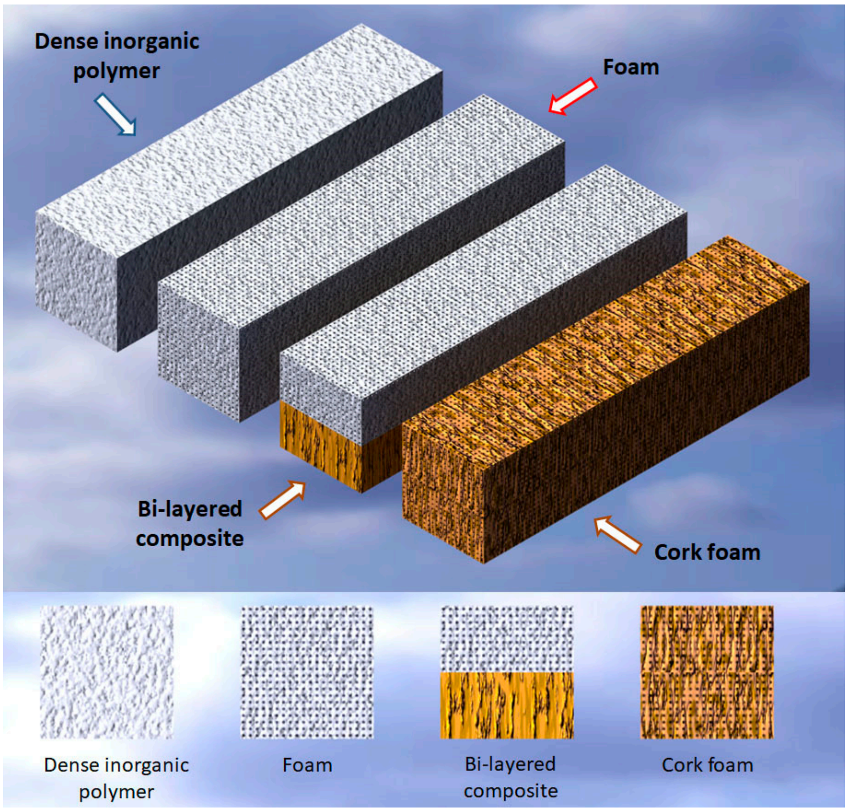


**Figure 1.** Schematic drawing of the distinct set of samples produced in this study: dense inorganic polymer, foams, bi-layered composites, and cork foams.

### 2.3. Materials Characterization

The samples' flexural and compressive strength was evaluated using a Universal Testing Machine (Shimadzu AG-25 TA; 0.5 mm/min). The tests were performed 28 days after synthesis on three samples per composition as defined in the standard protocol EN 1015-11:1999 followed in this study [29]. The samples were placed with the cork layer facing down.

The thermal conductivity was measured using 3 cubic specimens ($4 \times 4 \times 4$ cm$^3$) per batch by a heat flowmeter apparatus following standard ASTM C518-04 [25]. The specimen is placed in the middle of two parallel plates, and then a unidirectional heat flux across the sample is imposed by using heat flux transducers which establish a temperature gradient between the top and bottom plates, respectively set to 55 and 40 °C. The apparent density was calculated by the ratio between the mass and volume of the three cubic samples prior to their use in the thermal conductivity tests.

Scanning electron microscopy (SEM, Hitachi SU 70; energy-dispersion spectroscopy (EDS) Bruker) was used to study the cork granules and the inorganic polymers' microstructure, and the interface between the cork granules and the matrix. Prior to the SEM analysis the cork granules were coated with a thin layer of carbon, while a layer of sputtered gold/palladium was employed in the inorganic polymer composites to perform the EDS elemental mapping analysis.

## 3. Results and Discussion

### 3.1. Microstructural Characterisation of the Aggregate and the Inorganic Polymers

Figure 2 presents SEM micrographs of the cork granules used as light aggregates. As depicted, cork has a highly porous microstructure made by closed cells which explain their low apparent density (64 kg/m$^3$) and low water permeability.

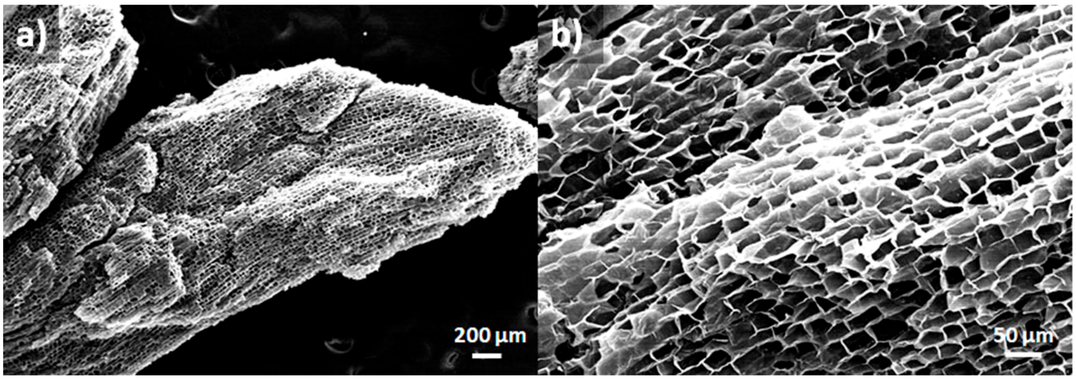


**Figure 2.** Scanning electron microscope (SEM) micrographs at two different magnifications (**a**,**b**) showing the microstructure of the cork granules.

Representative photographs of the various inorganic polymers (foams, cork foams and bi-layered composites) are provided in Figure 3. Figure 3a illustrates the influence of the foaming agent in the specimens' pore size, pore size distribution and volume of pores. As expected, increasing the foaming agent amount enhances the number and size of the produced pores, which will affect the thermal and mechanical properties of the foams (discussed in Section 3.2). The cork foams, shown in Figure 3b, present a homogeneous distribution of the cork granules in the binder regardless of the foaming agent content, showing that no segregation took place despite the much lower apparent density of the aggregates (64 kg/m$^3$) in comparison with the inorganic polymer paste (~1600 kg/m$^3$). Figure 3c shows the bi-layered composites formed by a porous upper layer, and by a cork-containing bottom layer, which is expected to endow thermal and acoustic insulation properties to the specimens [25]. The digital photographs of the bi-layered samples show a good interfacial connection between the layers demonstrating that the synthesis protocol is efficient, and that the amount of foaming agent in the top layer does not affect the adhesion between the two layers. The interface between the top and bottom layers was further evaluated using SEM and EDS line profile analysis and results for one selected sample (the higher porosity composition) are presented in Figure 4. The SEM micrograph shown in Figure 4a validates the macroscopic features depicted from the digital photographs, since a perfect adhesion between the layers is observed. The EDS line profile provided in Figure 4c shows the distribution of Si, Al and C within the layers. As expected, the Si and Al content in the upper layer is reasonably stable, the sudden drops are attributed to the presence of pores, while in the bottom layer the presence of C is associated with the presence of cork granules. The elements distribution in the sample is further illustrated by the EDS maps shown in Figure 4d,e.

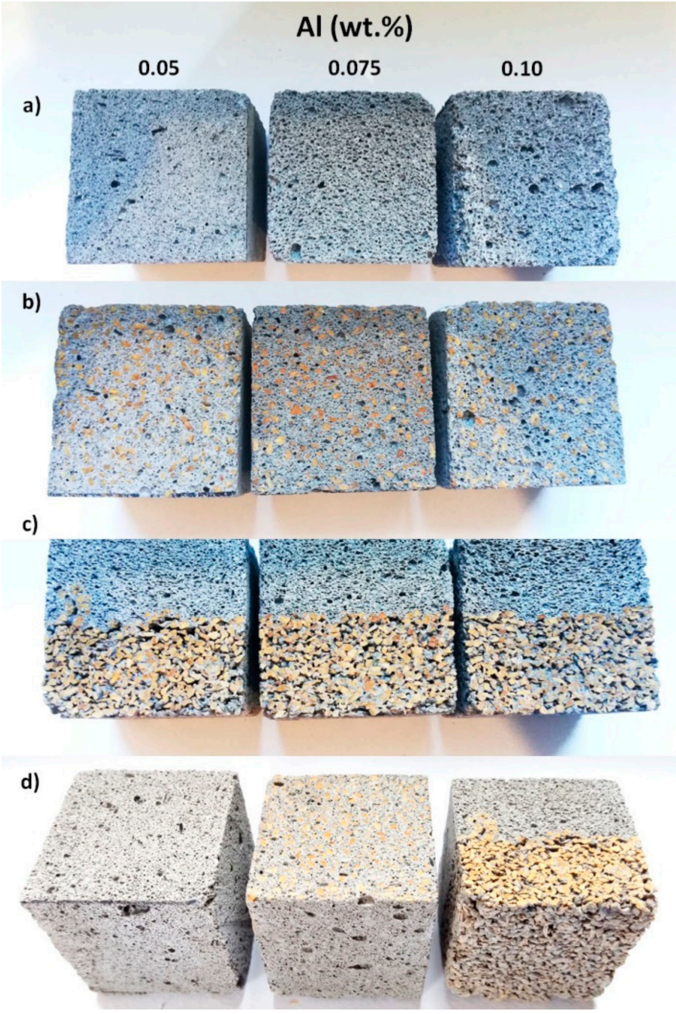


**Figure 3.** Digital photographs of the (**a**) inorganic polymer foams, (**b**) cork-containing foams, and (**c**) bi-layered composites containing varying amounts of Al. (**d**) shows a comparison between the three set of samples prepared using the same amount of Al (0.05 wt.%).

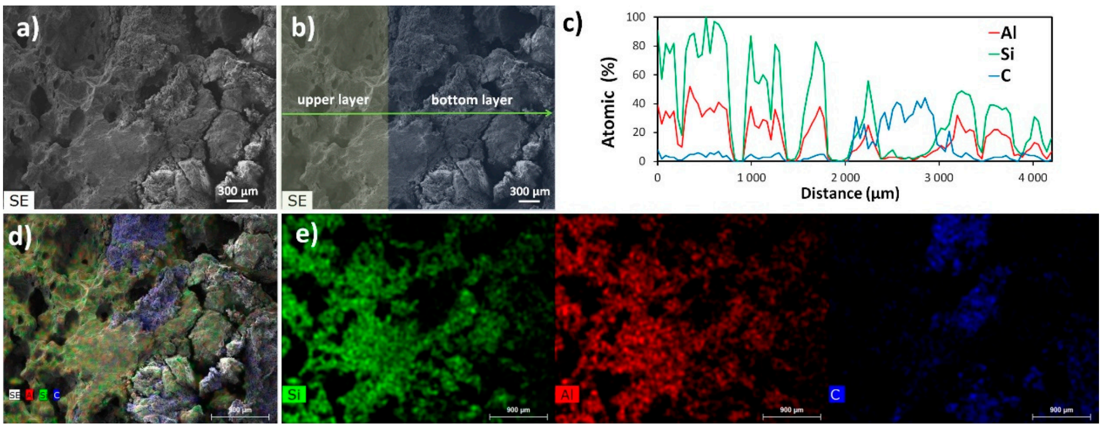


**Figure 4.** SEM micrographs (**a**,**b**), energy-dispersion spectroscopy (EDS) line profile (**c**) and elemental mapping (**d**,**e**) of the bi-layered composite prepared with 0.1 wt.% Al. In Figure 4b the two layers are identified using colors (porous upper layer—highlighted in light green; cork-containing (bottom) layer—highlighted in light blue) and the location and direction of EDS line profile identified by an arrow.

The interface between the aggregate and the matrix is a very important feature known to strongly affect the composites' mechanical properties [30,31]. The interface between cork and the inorganic polymer matrix was studied using SEM and EDS mapping and the results are presented in Figure 5. The SEM micrographs show the expected dense microstructure of the matrix, remaining equally dense at the vicinity of the aggregate. In fact, in our cork-composites no interfacial transition zone between the aggregate and the matrix was observed and this is corroborated by the higher magnification SEM micrograph given in Figure 5b showing a smooth connection between cork and the inorganic polymer matrix. The presence of cracks or voids was not observed in the areas surrounding the aggregates. The EDS map presented in Figure 5c shows a homogeneous distribution of the Si and Al, supporting the absence of an interfacial transition zone. These findings are in line with our previous work on cork–inorganic polymer composites [24,25], and with those reported when using natural siliceous aggregates [32], but differ from those reported for slag-based inorganic polymer mortars and concretes [31,33] which have reported compositional differences between the matrix and the area surrounding the aggregates. Nevertheless, in both studies a dense and compact microstructure in the interfacial transition zone was observed.

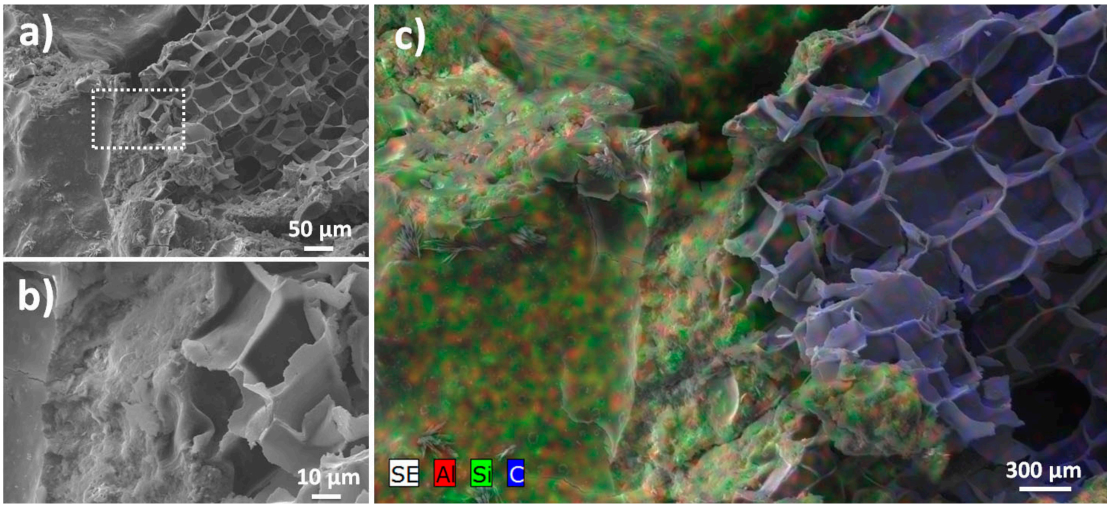


**Figure 5.** SEM micrograph at two magnifications (**a**,**b**) and corresponding EDS elemental mapping (**c**) for the cork-foam prepared with 0.10 wt.% Al.

### 3.2. Inorganic Polymer's Apparent Density and Thermal Conductivity

The influence of the mixture design (e.g., foaming agent and cork amount) and the synthesis route (e.g., foams; cork-foams and bi-layered composites) on the inorganic polymer apparent density is illustrated in Figure 6. The density of the reference composition (prepared without cork or foaming agent) is 1.17 g/cm$^3$. As expected, the addition of foaming agent to the compositions strongly decreases the specimens' apparent density, reaching 0.45 g/cm$^3$ in the higher porosity foam (prepared with 0.1 wt.% Al). Surprisingly, the density of the cork foams (containing 75 vol.% of cork) is similar to that seen in the foams prepared using the same amount of foaming agent but without adding cork. This unexpected result might be due to the mixing protocol in which the cork granules were added after the foaming agent to the slurries possibly disrupting the formation of gas bubbles and hindering their entrapping in the mixture.

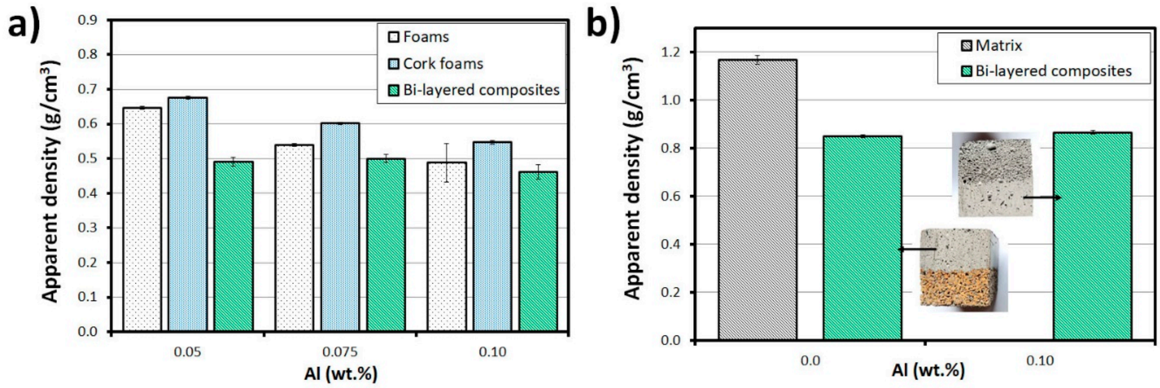


**Figure 6.** (**a**) Influence of the Al powder amount on the apparent density of the various compositions. (**b**) presents the apparent density of the matrix and of the bi-layered composites prepared without foaming agent and without cork. The microstructure of these bi-layered specimens is lustrated by the inset digital photographs.

As for the bi-layered composites, the porous/dense specimen prepared without adding cork to the bottom layer and adding 0.10 wt.% Al to the upper layer showed the highest density (0.87 g/cm$^3$). Interestingly, the other bi-layered sample having a dense layer but with a cork-containing layer instead of a porous layer showed similar density (see insets in Figure 6b). The addition of a minor amount of foaming agent (0.05 wt.%) to the sample's upper layer reduced their apparent density by a factor of 1.7 compared to the dense/cork-containing specimen, while higher amounts induced only minor fluctuations.

The thermal conductivity of the inorganic polymer specimens developed in this study is presented in Figure 7a. The matrix presents a fairly low thermal conductivity, and this is explained by the mixture composition which has been intentionally designed to produce low thermal conductivity materials. As expected, the addition of the foaming agent reduced the thermal conductivity of the foams, higher Al amounts inducing a stronger reduction. The cork foams show similar thermal conductivity in comparison with the foams, in line with their comparable apparent densities. The bi-layered composites showed the lowest thermal conductivity values demonstrating the interesting potential of this innovative material. The lowest thermal conductivity (94.9 mW/m K) was observed in the specimen containing the highest amount of foaming agent (0.1 wt.% Al) in its upper layer.

The lowest thermal conductivity seen for the bi-layered composites (94.9 mW/m K) was compared with other literature studies addressing the synthesis of lightweight inorganic polymers (foams and composites) and the results are provided in Figure 7b. As observed, the thermal conductivity of the bi-layered composites is much lower than most of the studies dealing with the addition of lightweight aggregates [14,20,21,34]; slightly lower than that seen for expanded waste glass [35] and expanded polystyrene waste composites [18]; being slightly superior to our previous works on cork-composites [24,25] due to the much smaller amount of cork used in the present study (75 vol.% instead of 90 [25] and 92 vol.% [24]), and 2.8 times higher than that reported for polystyrene-containing composites [19]. Moreover, the thermal conductivity of the porous/cork-containing composites is also much smaller than those reported for several other foams [36–40]; comparable to [41–47]; slightly higher than [48–51]; and much higher than that observed in [52,53]. The bi-layered composites' thermal conductivity, amongst the lowest reported to date for inorganic polymers, validates their use as energy-saving building material.

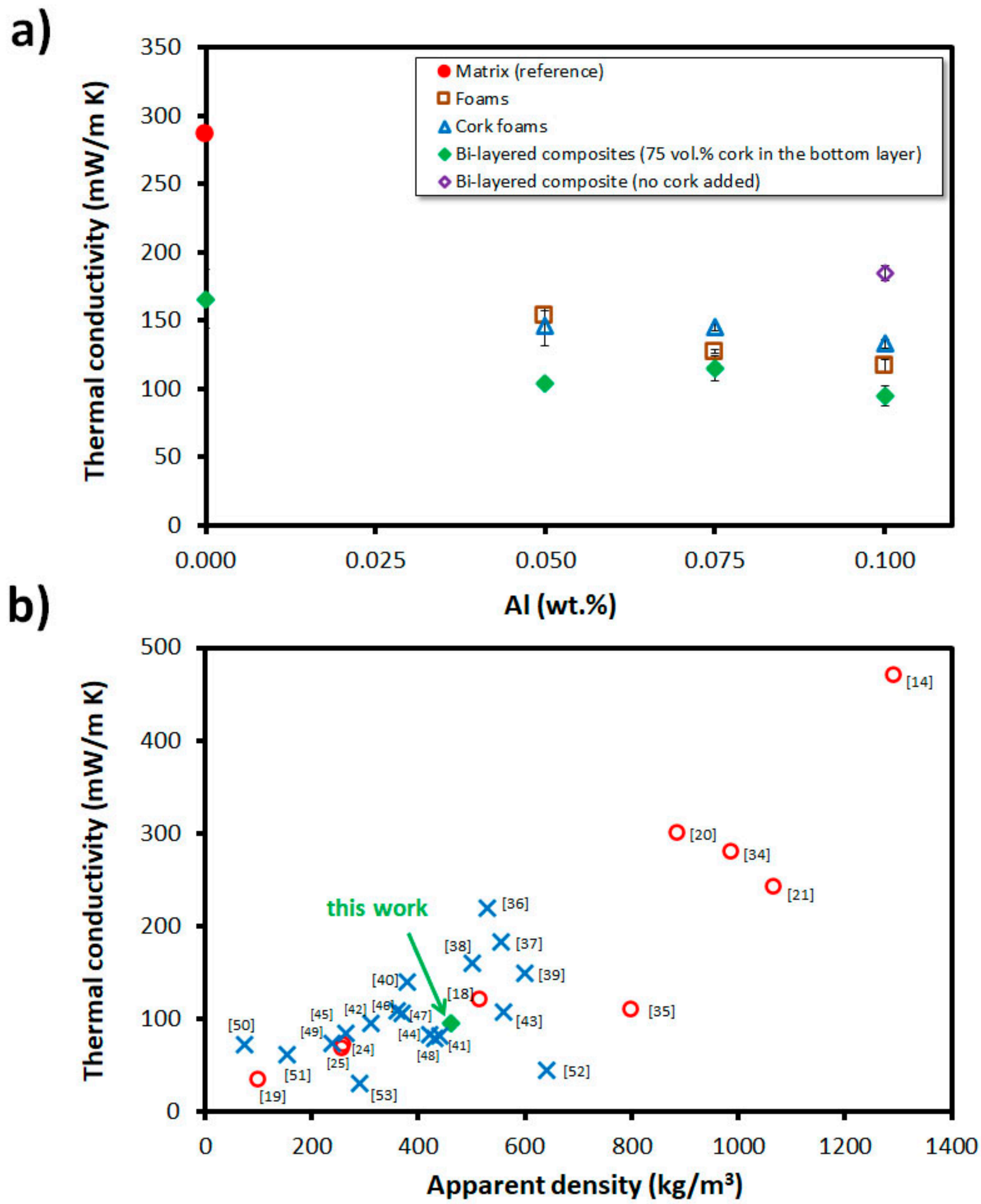


**Figure 7.** (**a**) Thermal conductivity of the various inorganic polymers produced in this study, and (**b**) comparison between the lowest thermal conductivity value here achieved for the bi-layered composite with literature studies concerning inorganic polymer foams (blue mark) and composites (red circle).

In addition to their low thermal conductivity, these composites are also expected to show other very desirable properties for building materials, such as moisture buffering ability and acoustic insulation properties [5]. In fact, the main idea behind the production of the bi-layered bodies, besides evaluating their feasibility as low thermal conductivity material, is the production of a multifunctional material capable of reducing the energy losses inside buildings while simultaneously regulating the indoor moisture fluctuation and providing sound absorption. We have previously shown that cork-composites can efficiently reduce energy losses, showing very high acoustic performance [25]. However, their moisture buffering capacity is much smaller than that exhibited by inorganic polymer foams [54]. The bi-layered composites coupling a porous layer with a cork-containing layer might be a perfect solution for this. Future work will evaluate the specimens' acoustic and moisture buffering properties. Porous materials with tunable properties, such as those produced here, are particularly attractive and might be used in a wide range of applications [55–57].

*3.3. Compressive and Flexural Strength Measurements*

The mechanical performance of the various inorganic polymers is shown in Figure 8. For comparison, the values observed for the bi-layered bodies prepared without adding foaming agent to the upper layer (left-side inset in Figure 8b) and for that prepared without adding cork to the bottom layer (right-side inset in Figure 8b) were included in Figure 8b,d. The reference composition (prepared without cork or foaming agent) reached a compressive strength of 24.8 MPa and a flexural strength of 4.1 MPa. All the lightweight specimens showed much lower strength. A strong decline (~eightfold reduction) in the samples' compressive strength was observed when adding 0.05 wt.% Al, and the strength further decreased when a higher level of foaming agent was added. Nevertheless, the higher porosity foam (produced with 0.10 wt.% Al) has a compressive strength of 1.2 MPa. Interestingly, the cork foams show higher strength (compressive and flexural) than the foams regardless of the Al content. The cork foams prepared with 0.05 and 0.10 wt.% have a compressive strength of 4.0 and 1.8 MPa, respectively, this being roughly 22% and 32% higher than their counterparts not containing cork. On the other hand, the bi-layered composites showed the lowest strength values. Nevertheless, the sample produced with 0.10 wt.% Al in the upper layer and 75 vol.% of cork in the bottom layer has a compressive strength of 0.93 MPa and a flexural strength of 0.84 MPa.

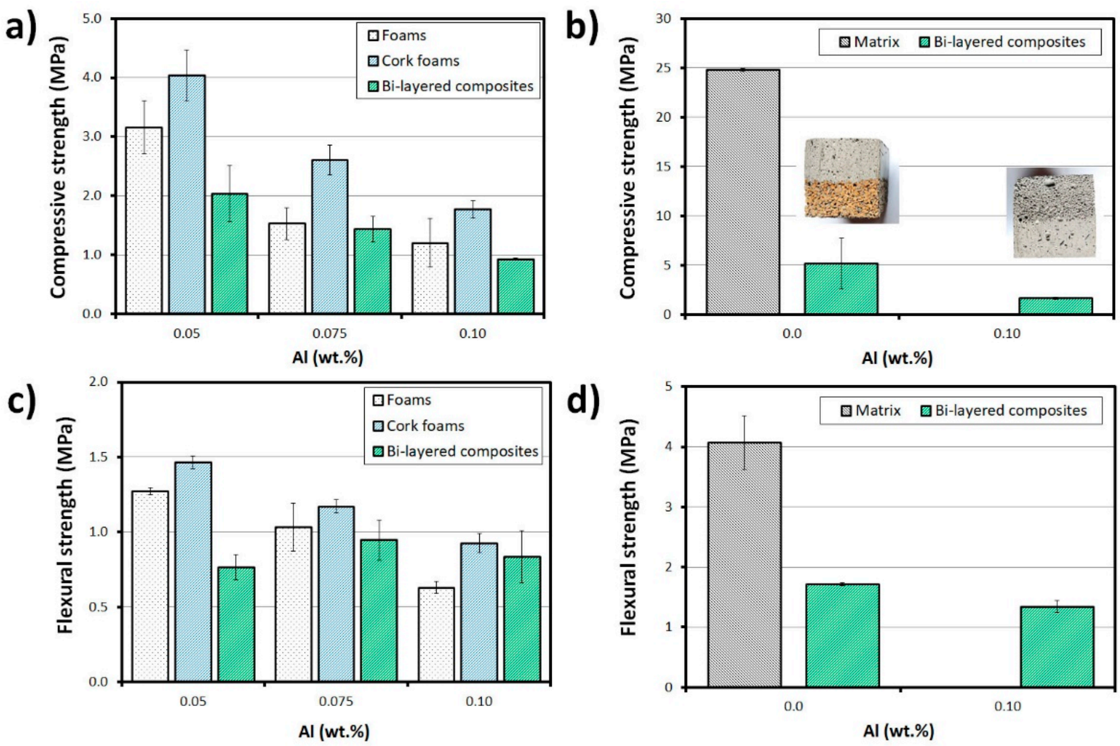


**Figure 8.** Compressive (**a**,**b**) and flexural (**c**,**d**) strength of the various inorganic polymers (measured at the 28th day).

The differences between the various compositions are further illustrated by plotting their compressive strength vs. apparent density, and results are shown in Figure 9. Not surprisingly, the decrease in the specimens' density, achieved by using a foaming agent, cork or a mixture between them, strongly reduces their compressive strength. The differences between the foams and the cork foams are also clearly illustrated, the cork foams showing higher strength and densities possibly due to their lower porosity caused by the addition of cork.

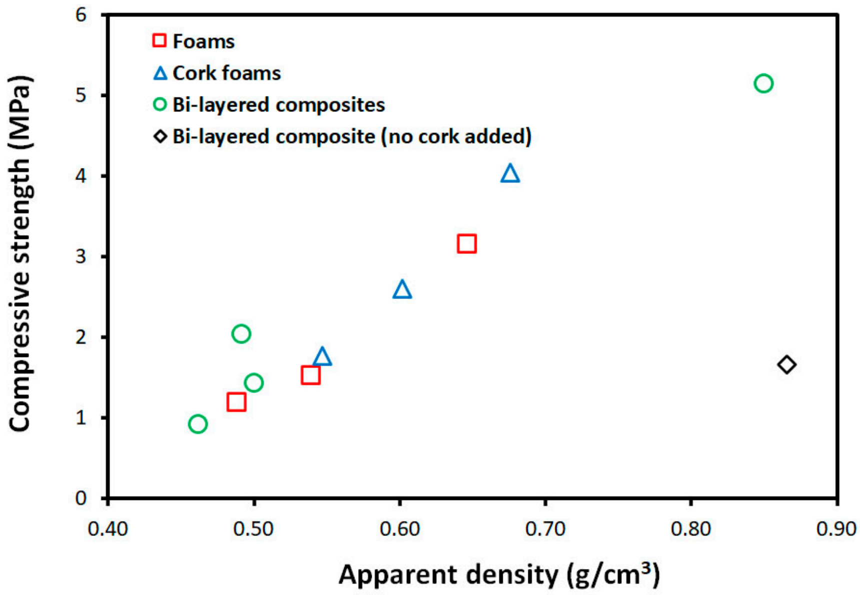


**Figure 9.** Correlation between the density and compressive strength in the lightweight inorganic polymers.

To further characterise the specimens' mechanical performance their specific strength was determined (ratio between compressive strength and density). The specific strength of the foams varied between 2.5 and 4.9 MPa $cm^3/g$, while higher values were seen in the cork foams, ranging between 3.2 and 6.0 MPa $cm^3/g$. The bi-layered composites showed a broader fluctuation, with values ranging from 2.0 (composition containing 0.10 wt.% Al) to 6.1 (composition containing 0.00 wt.% Al) MPa $cm^3/g$.

The compressive strength (0.93 MPa) of the lightest (461 $kg/m^3$) bi-layered composite here reported is superior to values reported for other low thermal conductivity inorganic polymers, such as those prepared using hydrogen peroxide as foaming agent (0.26 MPa) [41] and (0.78 MPa) [53], hydrogen peroxide coupled with air entrapping (0.26 MPa) or a cationic surfactant (0.57 MPa) [58], hydrogen peroxide coupled with calcium stearate (0.68 MPa) [51], and to those produced following a saponification route (0.2–0.4 MPa) [59], among others [45,47,48]. The lowest compressive strength exhibited by the cork foams (1.8 MPa) obviously surpasses all these studies, but also others including coconut-based (1.3 MPa) [52] and metakaolin-based foams (1.1 MPa) [40], and in addition is vastly superior to the other lightweight cork-inorganic polymer composites reported to date, (0.23 MPa) [24] and (0.15 MPa) [25].

## 4. Conclusions

In this investigation, different synthesis routes to produce lightweight inorganic polymers were compared, including the first ever production of a bi-layered cork-containing inorganic polymer. The cork foams showed higher mechanical performance than their non-containing cork counterparts (foams) having comparable, but slightly higher, thermal conductivity. The bi-layered composites, having a porous upper layer and a bottom cork-containing layer, reached the lowest thermal conductivity (94.9 mW/m K) which ranks them amongst the lowest values reported for inorganic polymers. In addition, their compressive strength (0.93 MPa) is superior to several other studies dealing with low thermal conductivity materials, further demonstrating the potential of this novel material produced at room temperature, using substantial amounts of an industrial waste (biomass fly ash) in the binder production, and cork (natural and renewable material) as light aggregate. Future work will evaluate the bi-layered composite's moisture buffer ability and acoustic performance.

**Author Contributions:** Conceptualization, L.S. and R.M.N.; methodology, L.S. and J.C.; validation, R.M.N., L.S. and J.C.; investigation, L.S. and J.C.; resources, J.A.L.; writing—original draft preparation, R.M.N.; writing—review and editing, R.M.N., L.S., J.C. and J.A.; supervision, R.M.N., L.S. and J.A.L. All authors have read and agreed to the published version of the manuscript.

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