

Functional Coatings and Surface Modifications in Cement–Matrix Composites

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The construction sector is one of the most active fields in the experimentation and research into new materials and applications capable of responding to the current needs for efficiency, energy saving, and eco-sustainability. Driven by these requirements, the sector is undergoing a rapid sustainable innovation introducing the use of eco-friendlier concrete materials, which implies a more efficient use of natural resources, embodied energy, waste circularity, and lower greenhouse emissions and production of industrial by-products [1]. Exploring the inherent state-of-the-art, most studies focused on the following two research topics.

1. Incorporating Waste Materials to Replace Virgin Aggregates in Cement Mixtures or Using Recycled Fillers as Eco-Efficient Reinforcing Agents

A massive amount of solid waste is generated by a variety of industrial activities, including mining, automotive, agriculture, power generation, iron and steel metallurgy, and manufacturing of electronic goods. Numerous hazardous solid wastes are flammable, chemically reactive, incendiary, corrosive, and contagious, and their discharge and landfilling have resulted in significant economic and environmental losses. Recycling or reusing solid wastes in cementitious mixes, such as aggregate substitutes, cement substitutes, or fillers, represents a valuable way to protect natural resources, mitigate carbon emissions, prevent the adverse disposal of wastes, and add new technological properties to concrete material [2]. Ceramic-based mining wastes (CMWs) in place of ordinary aggregates are recognized as viable solutions to improve the high-temperature performance and chemical durability of concrete without affecting its mechanical properties [3]. Polymer wastes (PWs), mainly plastics or rubber, as aggregates or fibers, represent a “green” strategy to produce lightweight cement and concrete mixes with improved toughness, ductility, impact strength, and thermo-acoustic insulation capacity [4]. Steel metallurgy by-products, such as steel slags (SSs), are characterized by a mineral composition very similar to cement clinker. Because of their active hydration ingredients, finer fractions are generally used as a mineral admixture for cement or concrete, while coarser fractions can be directly used as an alternative to natural aggregates in cementitious mixes. The presence of highly heat-conductive oxides in slag makes the concrete suitable for radiation shielding and self-sensing applications, showing better mechanical performance than traditional mixes [5]. Recycled reinforcement fibers (RRFs), including plastic fibers from municipal wastes, textile fibers from the fabric industry, metal fibers from end-of-life tires (ELTs), and natural fibers from agro-food by-products or residues, are implemented to replace virgin fibers in fiber-reinforced concrete. The presence of RRFs improves the concrete performance following a more eco-friendly route, by increasing its toughness, ductility, and impact and cracking resistance while reducing weight and density and, therefore, enhancing the high strength-to-weight ratio [6].



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2. Implement New Fiber-Reinforced Rebars (FRRs) as Substitutions for Steel

The steel industry is the leading productive sector regarding the production of reinforcement rebars for ultra-high-performance concrete (UHPC) applications. However, there is no doubt that the steel industry has been under tremendous pressure because of its environmental impact. It is one of the major producers of greenhouse gases, with its annual carbon dioxide (CO₂) emissions accounting for about 5% of the world's total. This is mainly a result of the energy requirement of blast furnaces, whose energy consumption accounts for about 70% of the process of steel production [7]. In addition, there is an important durability problem in steel-reinforced concrete members and structures: the corrosion of steel rebars embedded in them, which is the main source of damage and early failure of concrete structures that in turn create huge economical loss and environmental issues [8,9]. Ceramic-fiber-reinforced composites (glass, carbon, basalt) are gaining more and more interest in the construction industry to produce FRRs as internal reinforcements for concrete structures, with the aim of enhancing the durability and prolonging the serviceability of these members. Aside from being corrosion resistant, FRRs result in excellent thermo-mechanical properties, high strength-to-weight ratios (10–15 times greater than steel), excellent fatigue characteristics (about 3 times that of steel), and electromagnetic neutrality, and can be easily manufactured according to desired shapes and sizes, which makes it appealing as reinforcement for different structural elements such as beams, columns, and slabs [9,10]. In terms of environmental impact, a life cycle assessment (LCA) study conducted by Inman et al. [11] highlighted an about 60% saving in terms of climate change emissions when a composite reinforcement (specifically, basalt was analyzed in the cited paper) is chosen over conventional steel rebars, demonstrating the eco-efficiency provided by FRR technology.

Why Do Coatings Science and Surface Engineering Play a Crucial Role in This Research Framework?

Incorporating “unusual” constituents (waste aggregates, recycled fillers, and FRRs) into concrete mixes raises obvious compatibility issues with the surrounding cement matrix. Then, achieving proper compatibility and interface adhesion within the cement-based composite system is a key factor to make the effect of these alternative aggregates and reinforcements functional in terms of physical–mechanical behavior, durability, and structural integrity of the resulting composite, avoiding contributions such as “Achilles hell” rather than added values for the material. Considering the promising results that can be obtained by incorporating cement and concrete composites with waste aggregates/fillers and composite-based rebars, research interest is currently being directed towards the study and investigation of surface treatments and coating methods to ensure their adequate integration into the matrix.

Lightweight plastic and rubber waste aggregates have hydrophobic characteristics and relatively smooth and elastic surfaces, which are expected to weaken the interface compatibility (both chemical and physical) with the cement paste [12]. Physical, chemical, and “hybrid” (physical + chemical) surface treatments were proposed to enhance the interfacial bond between the PWs and the matrix. Physical treatments mainly include the pre-coating of the particles with a cementitious slurry with pozzolanic activity (cement, silica fume, limestone powder, and mortar). The result is a hydrophilic hard shell on the PW aggregate's surface that experiences better mechanical and chemical affinity with the surrounding cement paste [13]. The method proved to be highly efficient in terms of mechanical properties providing strength increase rates up to 98% with respect to uncoated particles [14]. However, the pre-coating phase makes the whole concrete material's preparation complicated and time-consuming [13]. Chemical treatments are primarily distinguished in (a) soaking with acid/alkali solutions and (b) treatment with silane coupling agents (SCAs). Soaking of waste polymer particles in chemical solutions (NaOH, acetone, KMnO₄) is performed to clean the dust and dirt on the particle's surface and increase its roughness and hydrophilicity [13]. The treatment mainly refers to rubber aggregates,

providing a rate of change in strength behavior up to +81% [15] depending on the type and molarity of the chemical solution. For instance, a NaOH-based treatment is commonly used to clean the surface of the particles from some hydrophobic chemical compounds (i.e., zinc stearate) used in the vulcanization of tires [16]. The use of highly aggressive chemicals inevitably leads to a negative impact in terms of environmental and human toxicity [13]. SCAs are organosilicon compounds that contain both organic and inorganic functional groups, reacting with inorganic substances (cement) and organic PW particles bonding after hydrolysis, so they can act as adhesion promoters at the polymer–cement interface, enhancing the adhesion between the two materials [17]. Li et al. [18] found a maximum increase in compressive strength of 43% by treating rubber aggregates with SCA. A recent work conducted by Wu et al. [19] revealed that recycled plastic aggregates pre-processed with SCA improve the strength of concrete by about 10% with respect to untreated particles. However, the eco-impact of using SCAs should be carefully addressed [13]. Ultraviolet (UV) radiation treatment (“hybrid”) represents a cleaner and cost-effective method for enhancing the interfacial adhesion between polymer aggregates and cement matrix. The basic physical principle is that the high radiative energy involved in UV radiations breaks chemical bonds in the polymer particle, easily producing free radical species. Free radicals can cross-link polymer chains and create new hydrophilic functional groups on the surface, ensuring better physical-chemical compatibility with the concrete [13]. However, a marginal increase in mechanical strength was detected in the literature using the UV-based method. Ossola and Wojcik [20] found that the exposure of tire rubber aggregates to UV-C for 20 h improved flexural strength by only 5% over that of the specimens containing untreated rubber. Fernández et al. [21] discovered that UV surface functionalization of plastic fibers (PET) does not produce significant changes in tensile strength and elastic modulus with respect to the properties reached by not-exposed fibers.

Although the ceramic waste aggregates have a chemical-mineralogical composition compatible with the cementitious matrix, extensive investigations were performed to improve their adhesion to concrete composites. CMWs, SSs, or construction and demolition (C&D) wastes need to be modified for the reasons of low structural quality, volume expansion, high porosity, and high water absorption [22]. Soaking these aggregates in pozzolan slurry or spraying with pozzolanic materials (fly ash, silica fume, nano silica fume) was recognized to be the most efficient technique to fill the pores on the aggregate’s surface, enhancing its compatibility with cement matrix [23]. Shaban et al. [23] investigated several formulations of pozzolanic slurries, finding improvements in the characteristics of recycled concrete aggregates in terms of lowering water absorption, increasing particle density, and lowering abrasion value. Malathy et al. [24] proved that the surface modification of SSs with fly-ash-based slurry reduced the open porosity and permeability of the aggregates, bringing benefits to the mechanical performance of the concrete as well as to its corrosion durability. A sophisticated method to improve the quality of waste ceramic aggregates is bio-deposition. Bio-deposition is based on the ability of specific bacteria to produce CaCO_3 on the surface of the cells in the presence of adequate Ca sources. CaCO_3 layer on the aggregate’s surface reduces the permeability and promotes hydration reactions, improving the density of the interfacial transition zone in the cement matrix [25]. Wu et al. [25] detected that bio-deposition effectively modified the properties of recycled concrete aggregates, reducing their permeability (30% reduction in water absorption compared with un-treated aggregates) and increasing the interfacial bond.

Coatings and surface modifications in fiber-reinforced concrete and UHPC play a key role in maximizing the contribution of embedded reinforcements on mechanical behavior. The stress transfer efficiency between these reinforcing components and the cement matrix is a prerequisite to improving the performance of reinforced concrete (tensile and flexural strength, fatigue life, ductility), as well as preventing premature debonding due to the internal stresses caused by the matrix shrinkage [26]. RRFs are generally pre-treated with the same methods used for virgin fibers. Chemical coatings based on SCAs, pre-treatments with acid/alkaline solutions, and surface modification with ozone are the

methods mainly implemented to improve the wettability of fibers with the cement paste [27]. In UHPC, the replacement of steel rebars with FRP changes the mechanism of load transfer between the concrete and the reinforcement. This is because FRRs are anisotropic: the shear and transverse properties are due to the resin, whereas their longitudinal properties are due to the fibers [28]. For this reason, surface treatments are necessary to ensure an adequate bond between the bars and the concrete. Different surface compatibilizing methods, including ribbing, helically wrapping, sand coating, and helically wrapping combined with sand coating were used to increase the bond force in concrete [29]. A comparative analysis of these treatments conducted by Štefanovičová et al. [29] revealed that helically wrapped FRRs performed better in terms of bond strength over the other surface treatments. The latest findings on the functionalization of reinforcing fibers and rebars in concrete involve the use of nano-coatings. Nano-silica coating was implemented by Bompadre and Donnini [30] to increase the tensile strength and the pull-out load of carbon fiber incorporated in textile-reinforced mortars. Nano-CaCO₃ coating was used by Yong et al. [31] to treat PVA fibers, aiming at enhancing the interfacial bonding properties of fiber-reinforced concrete. Basha et al. [32] coated glass FRRs with a nanoceramic layer with a gun-spray deposition method to improve the thermo-mechanical characteristics at high temperatures (up to 290 °C) of concrete reinforcement.

Based on the above, the research activity on functional coatings and surface treatments for “green” cementitious composites is broad and constantly evolving. The selection of the compatibilizing method must meet both performance and ecological requirements in order not to nullify the environmental aspect related to the implementation of more eco-friendly aggregates and reinforcements. The Special Issue “Functional Coatings and Surface Modifications in Cement-Matrix Composites” aims to explore new frontiers and to promote further research on coating treatments and surface modifications applied to recycled/waste materials and FRRs for their functional use in cement–matrix composites.

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