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Department of Chemistry and Biology "Adolfo Zambelli"

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Abstract

Synthesis of New Water Reducer Superplasticizers for building materials

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This industrial PhD project is focused on the development of new additives called Superplasticizers (SPs) that are particularly interesting for the engineering of construction field. These attracting molecules are organic compounds that are employed for building materials to improve their fresh workability capability and their mechanical properties in the hardened state. Their ability to disperse cement grains is due to their structure: they contain negatively charged functional groups that can interact with the positive charges present on the surface of the cement granules, thus avoiding the collapse of the cement particles and consequently making it fluid. Even if they are added in low quantity, they decrease the amount of needed mixing water and control the setting time without losing fluidity of the pastes, which results in higher strength and better durability of final materials.

Dispersants have given an important and fundamental improvement in materials engineering during the last century, in the late twenties the first-generation additives were developed from by-products obtained from the paper firm. Due their important applications in engineering field, research has been focused on the development of new and more performing plasticizers such as naphthalene/melamine sulfonate derivatives and polycarboxylate esters/ethers, that represent the second and third generation of additives.

To supply to the growing demand of new and more performing admixtures, the scientists have been pushing forward with breakthroughs in technology and knowledge. This PhD project fits into this contest and its aim is to provide innovative solutions for this framework.

At first, we propose a study[1,2] to investigate the role of new unconventional plasticizers on concrete, respect to the polymeric counterpart that are currently commercially available. In particular the attention was turned on the synthesis of

[1] Capacchione, C.; Talotta, C.; Neri, P.;Bruno, I.; Pauciulo, A.; Bartiromo, A.R.; Gliubizzi, R.; Gaeta, C. Synthesis of new Water Reducer Plasticizers for concrete, gypsum and clay. XXXIX National Conference of the Division of Organic Chemistry - SCI, CDCO, Turin (Italy), 8-11th September, 2019. Poster session.

[2] Capacchione, C.; Picariello, D.; Della Sala, P.; Talotta, C.; Neri, P.; Bruno, I.; Pauciulo, A.; Bartiromo, A. R.; Gliubizzi, R.; Gaeta, C. Dispersing and Retarding Properties of Water-Soluble Tetrasulfonate Resorcin[4]arene and Pyrogallol[4]arene Macrocycles in Cement-Based Mortar. *ACS Omega* **2020**, *5*, 18218–18225.

new macrocycles, based on resorcin[4]arene and pyrogallol[4]arene, functionalized with polar groups, such as sulfonate groups to increase their solubility in aqueous systems. The presence of negatively charged groups, linked to the pre-organized skeleton of the macrocycles, strongly influenced the cement conglomerate by modifying both the flowability of the cementitious paste and the setting time of the hardened product.

Even though the SP additives currently on the market show high performances, the challenge of our time is to study new types of innovative, eco-sustainable and highly performing super-plasticizers for future industrial applications. Prompted by these considerations we designed mPEG@β-cyclodextrin pseudorotaxanes[3] obtained by inclusion inside the cavity of the β-CD of a polymeric chain of PEG functionalized with carboxylic group. In fact, it is well known that in the highly alkaline environment of cement, the carboxylate groups act as anchor on, while the poly(ethylene oxide) side chains included inside the β-CD protrude from the cement surface into the pore solution to produce steric hindrance. From the analysis of their effect on mortar, these SPs were considered as new second generation additives.[3]

Finally, last part of the PhD project was carried on during the research period at the *Chair of Construction Chemistry and Polymeric Materials ChemPoWer under the supervision of the Prof. Andrea Osburg, Deputy Head of the F. A. Finger Institute for Building Materials Engineering at Bauhaus-Universität Weimar*. In detail, the aim of the abroad research period was to design, synthetize and evaluate the influence and the properties of new bio-based additives, starting from modified sugars like cellulose derivatives that were proposed in this thesis.[4] It was studied their synthesis and their possible application as new candidates for SPs for cementitious systems. Through the reduction of the dimension of the cellulose backbone and the introduction of anionic functional groups on their structure, it was

[3] Capacchione, C.; Della Sala, P.; Bruno, I.; Pauciulo, A.; Bartiromo,A.R.; Iannece, P.; Neri, P.; Talotta, C.; Gliubizzi,R.; Gaeta, C.; Poly(EtyleneGlycol)/β-Cyclodextrin Pseudorotaxane Complexes as Sustainable Dispersing and Retarding Materials in Cement-Based Mortar. *ACS Omega* **2021**, *6*, 12250–12260.

[4] Capacchione, C.; Partschefeld, S.; Osburg A.; Gliubizzi, R.; Gaeta, C.; Modified carboxymethylcellulose-based scaffolds as new potential ecofriendly superplasticizers with a retardant effect for mortar: from the synthesis to the application. *Materials* **2021**, *41*, 3569.

possible to observe their behaviour as superplasticizers: indeed, this kind of additives showed the capability to increase the flowability properties and the setting time of cement.