Received: 07.08.2023.
Accepted: 01.10.2023.

e-ZBORNIK Special Issue

Preliminary communication

Electronic collection of papers of the Faculty of Civil Engineering

https://doi.org/10.47960/2232-9080.2023.SI.13.1 ISSN 2232-9080

A new material applied to additive manufacturing technology through the revaluation of marble quarry waste with low environmental impact

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Abstract: Currently, in some marble quarries, the amount of waste amounts to 80%. The ReValoMur research project aimed to generate the necessary knowledge for the production of a new cementitious material, based on plastic waste from agriculture and waste derived from the extraction and/or transformation of natural stone, as a means of valorization of these industrial sectors in the Region of Murcia, in order to develop an optimal material of a more ecological scale within the productive range, focused on additive manufacturing as a potential technology for the rationalization and reuse of waste, that is, underused resources.

Key words: additive manufacturing, low environmental impact, revaluation, marble quarry waste, 3D printing

Novi materijal primijenjen u tehnologiji aditivne proizvodnje kroz revalorizaciju otpada iz kamenoloma mramora s malim utjecajem na okoliš

Sažetak: Trenutno u nekim kamenolomima mramora količina otpada iznosi i do 80%. Istraživački projekt ReValoMur imao je za cilj stvoriti potrebna znanja za proizvodnju novog cementnog materijala, temeljenog na plastičnom otpadu iz poljoprivrede i otpadu dobivenom iz eksploatacije i/ili prerade prirodnog kamena, kao sredstva valorizacije ovih industrijskih sektora u Regiji Murcia, kako bi se razvio optimalni materijal više ekološke razine unutar proizvodnog asortimana, usmjeren na aditivnu proizvodnju kao potencijalnu tehnologiju za racionalizaciju i ponovnu upotrebu otpada, odnosno nedovoljno iskorištenih resursa.

Ključne riječi: aditivna proizvodnja, mali utjecaj na okoliš, revalorizacija, otpad kamenoloma mramora, 3D ispis

1. OBJECTIVE

The ReValoMur research project aims to generate the necessary knowledge for the production of a new cementitious material, with the presence of plastic waste from agriculture and/or waste derived from the extraction and/or transformation of natural stone, as a means of valorization of these industrial sectors in the Region of Murcia, in order to develop an optimal material of a more ecological scale within the productive range, focused on additive manufacturing as a potential technology for the rationalization and reuse of underutilized resources (waste).

To contribute to the solution of the above described, the main objectives of this project were:

- Development of a methodology for the development of a new cementitious material based on agricultural plastic waste and/or waste derived from the extractive industry.
- Validation of this methodology by evaluating its viability in additive manufacturing.
- Development of a new cementitious material for additive manufacturing as a means of valorization of waste from industrial sectors in the Region of Murcia.
- To know the reduction of environmental impact resulting from the use of the new concrete compared to the use of traditional concretes.
- To valorize the traditional industries of the Region of Murcia, thus contributing to the establishment of the circular economy model.
- Contribute to the establishment of synergies of inter-sectorial collaboration between industries of the productive fabric of the Region of Murcia.
- To increase awareness among the agents involved in the target sectors about the use of emerging technologies and their contribution to the fight against climate change, pollution and waste of raw materials.

2. INTRODUCTION

2.1 State of the art of the most abundant plastic waste in the agricultural sector in the region of Murcia for use in cementitious conglomerates

The south-eastern part of Spain, between Murcia and Almeria, is one of the driest areas of the country, [1]. However, thanks to the use of agricultural plastics introduced in developed countries in the middle of the last century, this area is now one of the largest producers of fruit and vegetables in Spain and much of Europe, [2].

The plastic and agriculture sectors are closely linked due to the many benefits that the use of plastic has in agriculture, but not everything is an advantage, [3]. The use of plastics is generally associated with a potential negative impact on the environment, and recycling of plastics is therefore a priority, [4].

In the agricultural sector, the most commonly used plastics are those used to protect crops and to facilitate the harvesting of fruits and vegetables. Among the most common plastic protective elements are: plastic film for ground cover, shading netting, greenhouse plastic, harvesting bags and tree protection netting. In smaller quantities, but also with a considerable presence, we find plastic used in pipes and hoses, plastic bags for transporting large contents and plastic for packaging of phytosanitary products, [5].

Some of the most common types of plastic used for the manufacture of these elements are: low density polyethylene (LDPE), high density polyethylene (HDPE), polycarbonate, polypropylene (PP), polyvinyl chloride (PVC) and polyester (PE), [6].

All of them can become waste after their useful life and have a high impact on the environment due to their long degradation time. The incorporation of recycled polymers in mortars can also reduce the amount of plastic waste disposed of in landfills, thereby reducing their environmental impact.

The agricultural sector included recycling as a priority option years ago, within the operations and processes that are carried out. According to ANARPLA (National Association of Plastic Recyclers), in Murcia more than 30,000 tonnes of agricultural waste are generated each year, of which 75%-85% are recycled, [7].

Due to the need to find more sustainable and environmentally friendly ways of using plastic waste, one alternative is the addition of recycled polymers to mortars, which is becoming a widespread practice in the construction sector, [8], [9].

By adding ground or fibrous plastic particles to the mortar during the mixing process, including polyester, polypropylene and polycarbonate among others, the mechanical characteristics of mortars, such as compressive and flexural strength, [10], as well as their durability, can be improved. It has also been observed that mortars containing recycled polymers have lower permeability and water absorption, [11].

2.2 Different types of waste from the extractive and/or stone processing industry in the region of Murcia for use in recycled concrete and mortar mixes

Currently, among the biggest problems facing the natural stone sector in terms of waste generation are the generation of sludge, stone dust and rock tailings from quarries during quarrying, [12], [13].

Sludge from natural stone quarrying is the most common waste generated during the quarrying and processing of natural stone, [14]. The composition of sludge generated in the stone industry can vary depending on the type of stone being processed, the method used to extract and process it, as well as the measures that have been taken to reduce sludge generation. However, in general, sludge from the stone industry is usually composed of a mixture of water and fine stone particles resulting from the cutting, polishing and processing of natural stone, [15]. These stone fragments can contain a variety of substances, including clay, mica, quartz, iron oxides, feldspar, silica and other carbonates. A large percentage of these sludges end up in landfills or are used as backfill on land and roads, but are not used as a raw material to manufacture new commercial products. In small quantities, it is used by cement producers to make cement, concrete and mortar, and is also used in the paper, paint and ceramics industries, [16].

In the Murcia region, as in other regions, the stone quarrying and processing industry can generate various types of waste that can be used in recycled concrete and mortar mixes. Both by-products could be introduced into these mixtures after being completely dried and subsequently ground.

2.3 State of the art in the specific field of production of concrete based on plastics and marble waste and its application to additive manufacturing

Research in the construction sector with the aim of optimizing processes, reducing costs, improving performance and taking into account environmental sustainability has become increasingly effective in recent years. Although the construction sector has been characterized by very slow progress in the application of technology in construction processes compared to other productive sectors, the digital revolution is here to stay.

From the point of view of environmental impact, numerous studies have been carried out in recent years on the use of industrial waste and recycled materials in the manufacture of concrete. Research on the addition of certain materials has led to changes in the properties of concrete, cost reductions and specific effects depending on the type of material and dosage, [17].

To improve the properties of mortars, plastics can be incorporated into them in various ways. During the mixing process, one of the most popular methods is to add plastic additives to the mortar, [18]. Chemical substances known as plastic additives are added to mortar to increase its workability, plasticity, strength and durability, [19]. Many different types of additives can be used, including polyethers, polycarboxylates and acrylic polymers. While mixing the mortar, the plastic admixture is combined with the other ingredients, including cement, sand and water. The plastic admixture functions as a water-reducing agent, which means that it reduces the amount of water needed for mixing, which increases the strength of the mortar and, as a result, reduces porosity, [20].

Plastics can be incorporated into mortars by adding plastic fibres in addition to plastic admixtures. When combined with the other mortar ingredients, these fibres increase the mortar's tensile, flexural and fatigue strength, [21].

3. TESTS

The main objective of this research has been the evaluation of the feasibility of the total or partial substitution of the fine addition provided by the limestone filler in 3D printing mixtures, as well as the possible incorporation of plastic waste. This was particularly interesting as, being sludge captured from marble dust, despite its rocky appearance, it is a pulverulent formation that requires separation milling.

For the formulation of the 3D printing mortar, Cementos Cruz CKLEEN cement has been used as a reference due to its low clinker content, which allows to obtain higher 3D printing open times and to limit cracking due to hydration heat. In addition, limestone aggregate fractions with a maximum particle size of 2mm and limestone filler have been incorporated to increase the percentage of fines by 11%. The WCR (Water-Cement Ratio) percentage was set at relatively low percentages, which is expected to result in high strengths.

Below can be seen the different tests carried out by Cementos Cruz with the dosage of cement in the base, aggregate 02 and marble dust on the surface.

Table 1. Summary of the different mixes carried out

001_CTM3D CKLEEN Cement Aggregate 02 Limestone filler Liquid water-reducing additive Solid cellulose	**002_CTM3D** CKLEEN Cement Residue polymer Limestone filler Liquid water-reducing additive Solid cellulose	**003_CTM3D** CKLEEN Cement Marble dust Limestone filler Liquid water-reducing additive Solid cellulose
004_CTM3D CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive Solid cellulose	**005_CTM3D** CKLEEN Cement Polymer residue Marble dust Limestone filler Liquid water-reducing additive Solid cellulose	**006_CTM3D** CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive Solid cellulose
007_CTM3D CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive 2 Solid cellulose	**008_CTM3D** CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose	**009_CTM3D** CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive 4 Solid cellulose

010_CTM3D CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive 5 Solid cellulose	**011_CTM3D** CKLEEN Cement Aggregate 01 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose	**012_CTM3D** CKLEEN Cement Aggregate 01 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose
013_CTM3D CKLEEN Cement Aggregate 01 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 3	**014_CTM3D** CKLEEN Cement Aggregate 01 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 4	**015_CTM3D** CKLEEN Cement Aggregate 01 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5
016_CTM3D CKLEEN Cement Aggregate 01 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5 Residue polymer	**017_CTM3D** CKLEEN Cement Aggregate 01 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5 Residue polymer 2	**018_CTM3D** CKLEEN Cement Aggregate 01 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5 Residue polymer 3
019_CTM3D CKLEEN Cement Aggregate 01 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5 Residue polymer 4	**020_CTM3D** CKLEEN Cement Aggregate 01 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5 Liquid lignosulphonate	**021_CTM3D** CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5 Residue polymer
022_CTM3D CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5 Residue polymer 2	**023_CTM3D** CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5 Residue polymer 3	**024_CTM3D** CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5 Residue polymer 4
	025_CTM3D CKLEEN Cement Aggregate 02 Marble dust Limestone filler Liquid water-reducing additive 3 Solid cellulose 5 Residue polymer 5	

The polymer most used in this project was PET, as it is the most abundant in agriculture. Modifications were made to the 008_CTM3D formula in proportions of 5, 10, 15, 15, 20 and 25%, with the best result being the 021_CTM3D mixture, which had a PET content of 5%, but still performed significantly worse than the 008_CTM3D sample.

4. RESULTS OF THE MIXTURES

Once the mixes had been made, tests were carried out to rule out some of the proposed compositions. For this, the fluidity in shaking table, open time, water-cement ratio and also qualitative tests were taken into account, such as whether the mixture fluidises with energy and without it does not. Also, as can be seen below, the stackability test was carried out with a spray gun and with portions of paste.

After fresh state testing of the 20 formulations, 4 candidates were selected for their good thixotropic performance in the fresh state, making them good candidates for 3D printing.

The fresh state results of the samples that gave the best rheological results, and therefore have been selected for further testing, correspond to formulae 005, 008, 015 and 020.

Table 2. Characterization of the best performing mixtures

FRESH STATE_CTM3D	005_CTM3D	008_CTM3D	015_CTM3D	020_CTM3D
OPEN TIME	65 min	80 min	70 min	90 min
THIXOTROPY	Very good	Excellent	Very good	Good
STACKABILITY (GUN TEST)	5 layers	12 layers	7 layers	4 layers
DISINTEGRATED APPEARANCE	Homogenous	Homogenous	Homogenous	Homogenous
ADHESION	Correct	Correct	High	Excessive

After carrying out the different formulations and the spray gun test, most of the mixtures based on the reuse of different plastics from agricultural waste had to be discarded, as they did not give good results. Only mix 005_CTM, which did not incorporate aggregate, gave acceptable results with polymers in its composition.

The rest of the mixtures were made starting from the 008_CTM mixture, which a priori, was the one with the best behavior in fresh state. PET waste was introduced into the mixes in proportions of 5, 10, 15, 15, 20 and 25%. The one that gave the best result was the one that incorporated 5% (021_CTM) and its behavior was significantly worse than that of 008_CTM.

Finally, triple moulds were made from the 4 selected formulas, 005_CTM, 008_CTM, 015_CTM and 020_CTM. These moulds were left to cure for 28 days, after which flexural and compressive strength tests were carried out.

The results obtained after subjecting the selected samples to the bending and compression tests are shown below.

Table 3. Results of the flexural and compression tests of the specimens made with the different mixtures

FRESH STATE_CTM3D	005_CTM3D	008_CTM3D	015_CTM3D	020_CTM3D
BENDING (28 DAYS)	3,2 MPa	8,6 MPa	4,6 MPa	2,8 MPa
COMPRESSION (28 DAYS)	31 MPa	46 MPa	23 MPa	19 MPa

After seeing these results, it was concluded that the 008_CTM3D formula is the most suitable to evaluate in full scale 3D printing due to its good behavior in the fresh and hardened state and it was decided to evaluate the real printability of the 008_CTM3D mix using the Cartesian printer of the 3DLAB of Cementos Cruz.

The components of the 008_CTM3D mixture in more detail expressed in percentages can be found below.

Table 4. Composition of the best performing mixture

008_CTM3D	% WEIGHT IN THE MIXTURE	% FINE MIX
CKLEEN Cement	29,07	29,07
Aggregate 02	54,40	9,25
Marble dust	11,20	11,20
Limestone filler	5,30	5,30
Liquid water-reducing additive 4	0,03	0
Solid cellulose	0,10	0
WCR	25	

5. PRINTING RESULTS

In order not to rely solely on the laboratory data obtained, it was decided to carry out the printing to ensure the efficacy of the selected mixture. As can be seen below, the printing was successful.

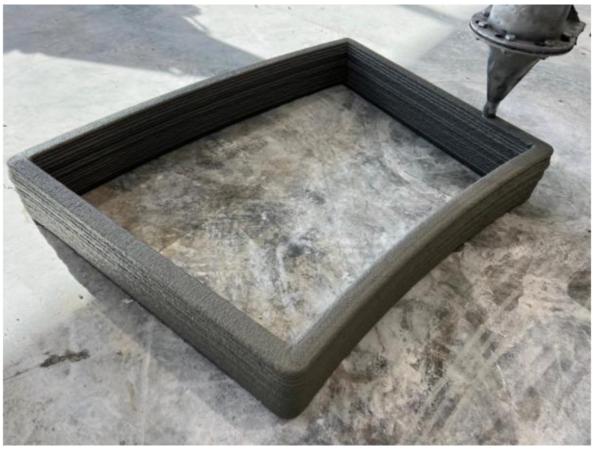

Figure 1. 3D printing with the mixture 008_CTM

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