APPLICATION OF RESINOUS BINDERS WITH INCORPORATION OF CARBONATED SLUDGES FROM THE DIMENSION STONE INDUSTRY IN THE PRODUCTION OF STONE COMPOSITES

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INTRODUCTION

The carbonated dimension stone extractive and processing industry produce high amounts of wastes that are deposited in the open in heaps and deposits of carbonated sludge (Fig. 1).
The industrial application of this waste makes it possible to add value, transforming it into a by-product, thus contributing to the framing of the limestone and marble extractive and processing sub-sectors, in the "Action Plan for the Circular Economy", promoting the sustainable growth. By this means, this research has shown that the recycling slurries as a raw material are possible to integrate binders production through its incorporation on the manufacture of ornamental stone composite materials, partial or totally replacing the epoxy resins traditionally used in this type of products.

Fig. 1. Deposit of carbonated sludge in the factory Criamármore - Mármores Portuguesas, Lda

MATERIALS

The slurries were sampled in the filter presses plants at the companies: António Galego & Filhos – Mármores SA, referred to as M(AGF) and A.L.A. de Almeida SA, referred to as M(A). The limestone carbonated sludge was collected at Solancis - Sociedade Exploradora de Pedreiras SA, referenced as C(S) and MVC - Mármores de Alcobaça Lda., referenced as C(MVC).

RESULTS & DISCUSSION

Sludges - Chemical Characterization

The chemical analyses (Table 1) carried out using atomic spectrometry revealed a fundamentally carbonated material. All carbonated sludges have significant percentages of CaO and show relevant percentage of loss of ignition.

Table 1 – Chemical analysis.

Samples	CaO (%)	SiO_2 (%)	MgO (%)	Loss on Ignition (%)
M(AGF)	45,504	2,549	3,156	42,97
M(A)	51,555	3,537	0,829	42,15
C(MVC)	52,580	0,357	0,337	43,50
C(S)	54,189	0,297	0,301	43,30

Formulation of Binders Consisting of Carbonated Sludge and Resin

Table 2: Results of uniaxial compressive strength tests after 28 days of curing.

Formulations %	R (MPa)
ANM3 – 54,43%NM / 45,57%Res.	102.73
ANM4 – 50%NM / 50%Res.	98.35
ANM5 – 47%NM / 53%Res.	96.23
ANM6 – 52%NM / 48%Res.	106.37
ANC3 – 52,31%NC / 47,69%Res.	103.20
ANC4 – 50%NC / 50%Res.	102.12
ANC5 – 47%NC / 53%Res.	96.04

NM – Marble sludge; NC – Limestone sludge; Res – Resin.

The mechanical characterization of the binder was carried out by evaluating the resistance to uniaxial compression of the different formulations with different percentage contributions of limestone and marble sludge and resin. The specimens kept for curing in air and were tested at 7, 14 and 28 days, with increasing uniaxial compressive strength over this period, reaching higher uniaxial compression values at 28 days (Table 2).

Composite Formulations with Binder 52/48 and Marble Aggregates

Having defined the formulations with the best performance, in terms of uniaxial compressive strength tests (NP EN 1926-2008) (Table 3), the remaining characterization tests were made, namely:
i) determination of flexural strength under concentrated load;
ii) apparent density and porosity (NP EN 1936-2008);
iii) absorption of water at atmospheric pressure (NP EN 13755);
iv) absorption of water by capillarity (NP EN 1925-2000).

Table 3: Stone composite formulations and uniaxial compressive strength test results for the several formulations.

Formul.	Aggregates			Binders			Average uniaxial Compression Strength (MPa)
	BA	B1	B2	NC	NM	Res	
F1	30%	30%	40%	52%		48%	73.30
F2	20%	20%	60%	52%		48%	69.06
F3	35%	15%	50%	52%		48%	61.11
F4	40%	40%	20%	52%		48%	**91.96**
F5	30%	30%	40%		52%	48%	52.26
F6	20%	20%	60%		52%	48%	76.33
F7	35%	15%	50%		52%	48%	81.20
F8	40%	40%	20%		52%	48%	**88.19**

Table 4: Characterization tests for the binders.

		i	ii				iii	iv
Curing (Days)	Binder	Flexural strength (MPa)	Open pore Volume (ml)	Apparent volume (ml)	Apparent density (g/m³)	Open porosity (%)	Water absorption at atmospheric pressure (%)	Average (g/m²s)
28	Marble	1549 ± 1.38	0.22 ± 0.03	117.0 ± 7.0	2.279 ± 0.014	0.19 ± 0.02	0.2 ± 0.03	0.088 ± 0.010
	Limestone	13,49 ± 0.97	0.21 ± 0.04	104.6 ± 7.4	2.263 ± 0.017	0.20 ± 0.03	0.1 ± 0.03	0.062 ± 0.019

The marble aggregate, supplied by the company *Marvisa, Mármores Alentejanos Lda.*, consisted of three types, with the following granulometric intervals: BA (4 mm / 6.3 mm), B1 (8 mm / 14 mm) and B2 (14 mm / 25 mm) (Table 3).

NEW RESULTS

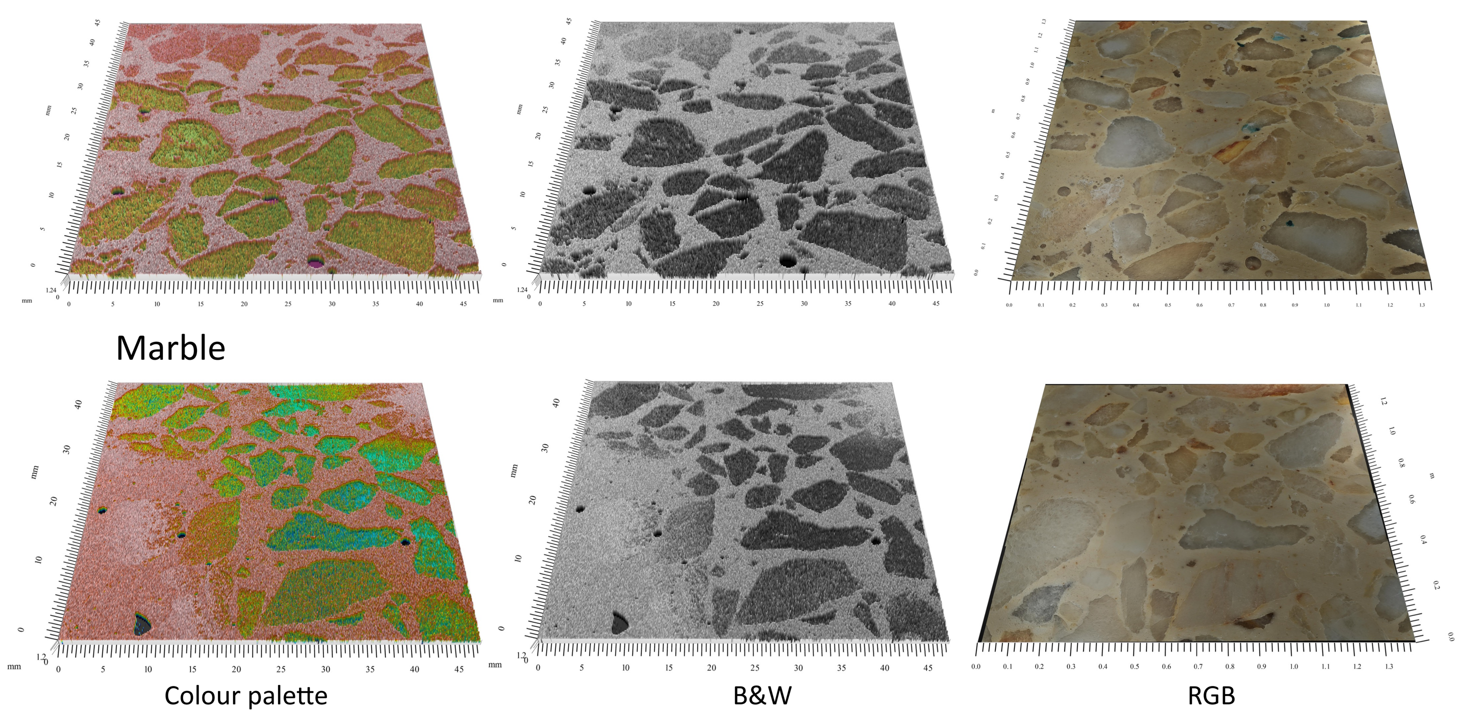

Fig.2. Micro-topographic maps of limestone and marble sludge binder.

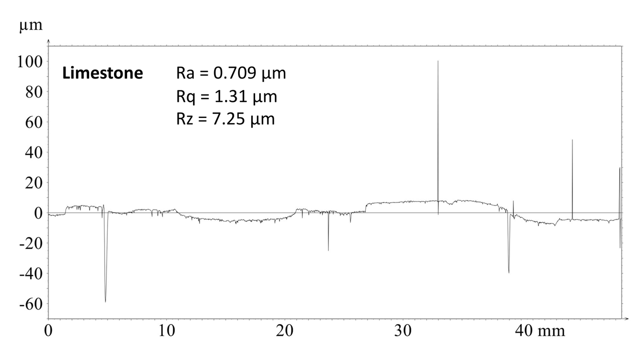

Fig. 3. Roughness profile of limestone sludge binder.

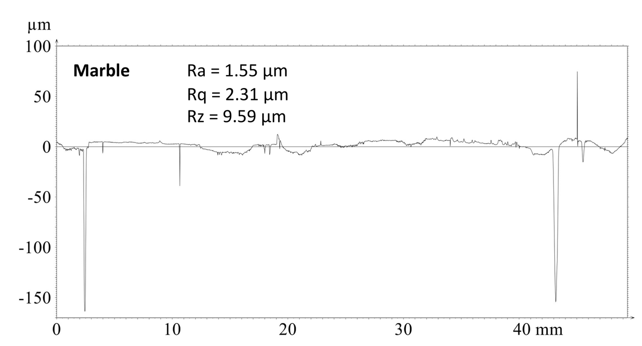

Fig. 4. Roughness profile of marble sludge binder.

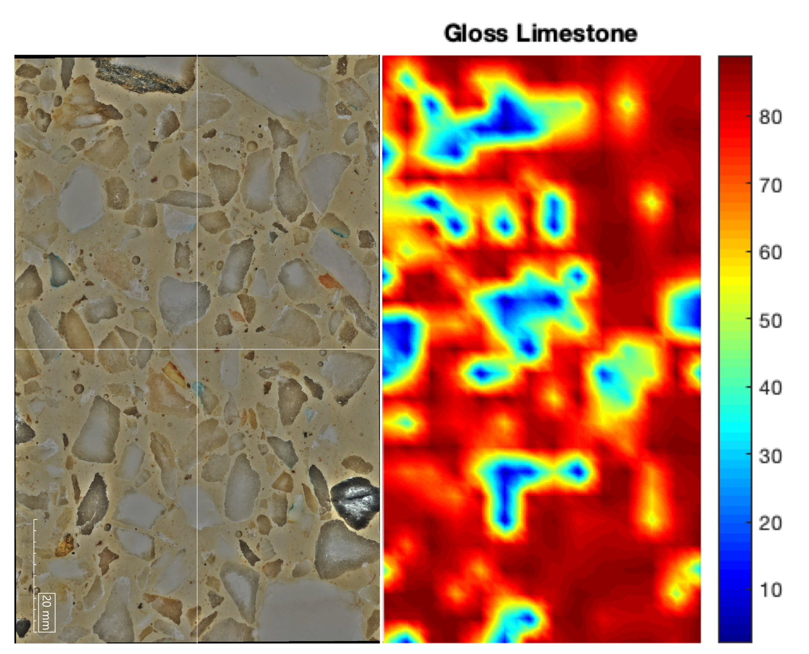

Fig. 5. Gloss maps on polished surfaces of limestone sludge binder.

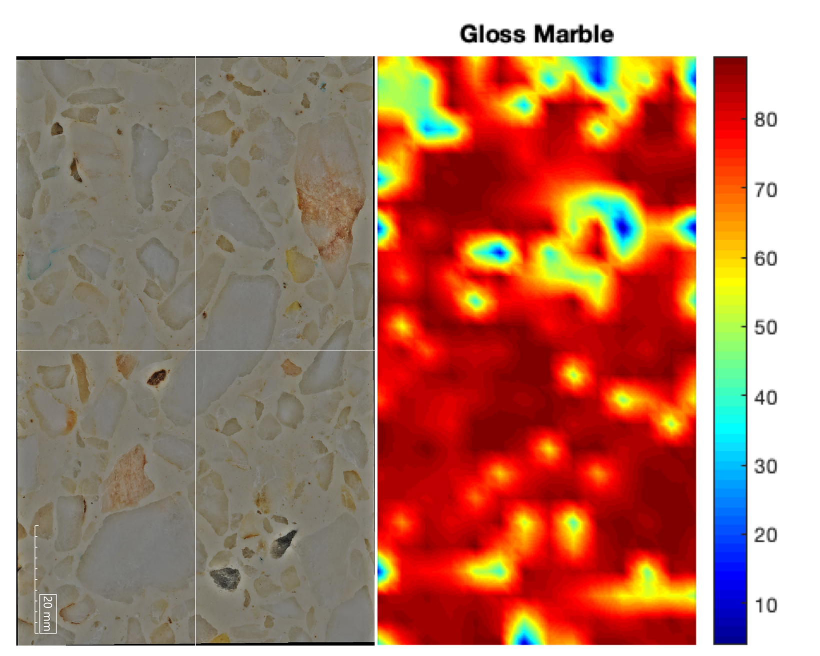

Fig. 6. Gloss maps on polished surfaces of marble sludge binder.

CONCLUSIONS

The use of polyester resin in replacement of epoxy resin seems feasible. The price of epoxy resin is on average four times higher than polyester resin, which makes stone composite products substantially more expensive.
As one goal of the investigation was the reduction of resin and its partial replacement by carbonated sludge, the investigation gradually incorporated successively higher percentages of solid load, without compromising the strength of the specimens. Thus, the ideal binder percentage was: 52% carbonated sludge and 48% polyester resin.
The results obtained in the compressive and flexural strength tests are promising, given the fact that the formulations were carried out manually using a manual mixer.






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REFERENCES

Afonso, P.; Azzalini, A.; Faria, P.; Lopes, L.; Martins, R.; Mourão, P.; Pires, V. (2023). Mortar Based on Sludge from Carbonate Dimension Stone Processing Industry - an Experimental and Feasibility Approach. 2023 Geo-Resilience Conference. The British Geotechnical Association
Catálogo da Pedra Portuguesa. Assimagra: Recursos Minerais de Portugal, consulted on April 15, 2023 https://www.assimagra.pt/images/publicacoes/Cat%C3%A1logo-da-Pedra-Portuguesa_2012-compactado.pdf,
DGGM (1992). Ministério da Indústria e Energia, Direcção Geral de Geologia e Minas. Catálogo de Rochas Ornamentais Portuguesas. Vols. 1 - 4
Germano, D.; Lopes, L.; Gomes, C.; Santos, A.; Martins, R. (2014). O Impacte das Pedreiras Inactivas na Fauna, Flora e Vegetação da Zona dos Mármores: Problema ou Benefício? *Callipole* – Revista de Cultura. 21, 149-171. Câmara Municipal de Vila Viçosa
LNEG. Portal de Rochas Ornamentais Portuguesas. https://geoportal.lneg.pt/pt/bds/rop/, consulted on April 15, 2023
Juvandes, L.F.P. (2002). Materiais Compósitos Reforçados com Fibras, FRP. Ciência dos Materiais, Licenciatura em Engenharia Civil, Faculdade de Engenharia da Universidade do Porto, Departamento de Engenharia Civil, pp. 76.

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