Valorisation of waste marble powder as additive of epoxy polymers for the protection of commercial marbles

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Marble is a material that has been used since antiquity as a building material, with a range of uses that extends from small structures to grand monuments that exist for centuries. Despite its particularly good properties, marble is vulnerable to various corrosive environmental factors (e.g., acid water and solvents) and it is necessary to protect it with anti-corrosion agents. Another problem in marble industry is the breaks and other types of damages that occur during the processing or transporting of the material, resulting in significant financial losses. Apart from the processing difficulties of marble, another problem of the marble industry is the increasing amounts of waste marble powder (WMP) due to higher production rates through the last years, leading in deterioration of environmental pollution (Demirel and Alyamaç, 2018). WMP is a by-product of marble cutting and polishing processes, that can not be stored and should be utilized in other sectors.

To prevent marble damaging during processing and transporting, the use of protective agents has been implemented, which are either impregnated into the marbles to increase the consistency of the structure or used as coatings for corrosion protection. In their majority, the protective agents are polymeric materials and mainly epoxy resin/hardener systems, which have excellent thermal and mechanical properties, dimensional stability, transparency, good processing time, while their properties can be adapted at will by selecting an appropriate combination of monomers – system components (Kumar et al., 2018). Despite the exceptional properties of epoxy polymers, there are some points in their use as protective agents of marble that could be improved, leading to a significant increase in the quality and commercial value of marble products. The most important of these points are colour resistance to UV radiation, non-discoloration of surfaces to which they are applied, resistance to corrosion and chemicals, appropriate rheological properties better penetration into the structure imperfections, reduction of liquid and gas permeability.

The aim the present work is to study the potential use of WMP as an epoxy polymer additive and the production of a composite resin with improved marble protection action compared to the respective neat epoxy polymer. The benefits of an approach like this are manifold, as WMP, a by-product of marble industry, will be used to improve the properties of the final commercial products of the same industry. This way, economic losses can be reduced and environmental pollution can be prevented. To achieve this purpose, WMP of Thasos marble was used to produce composite polymers with a system of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin and amine curing agent. The produced composite material was applied to pieces of Thasos marble slabs and its protective properties were tested in comparison with those of the neat epoxy polymer. More specifically, WMP was used both as it was produced and after particle size reduction/homogenization via ball-milling in various concentrations. Concerning the characterization of WMP, morphology and particle size were examined via scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), structure and chemical composition were determined via Fourier transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD), while thermal properties were determined via thermal gravimetric analysis (TGA). As it concerns the properties of pristine epoxy polymer and WMP composites, dynamic mechanical analysis (DMA) was used to determine the thermomechanical properties, differential scanning calorimetry (DSC) was used to determine the thermal properties, XRD was used to study the structure of the composites, while tensile, flexural, impact and compression tests were used to determine the mechanical properties. Finally, polymer coated marble specimens were exposed to UV light to test their color retention against UV radiation.

XRD patterns of Thasos WMP are presented in Figure 1. The identification and quantification of phases revealed that Thasos marble consists of 96.1 % dolomite and 3.9 % calcite. Figure 2 shows a SEM image of unprocessed WMP. The marble powder consists of particle agglomerates with variable size (up to ca. 100 μm), while the primary particles are of irregular shape and significantly smaller size. The elemental analysis results of the sample depicted in Figure 2 are shown in Table 1. Spectrum 8 values are characteristic of dolomite, while the results of Spectrum 6 and 7 lay between the values of dolomite and calcite structure.

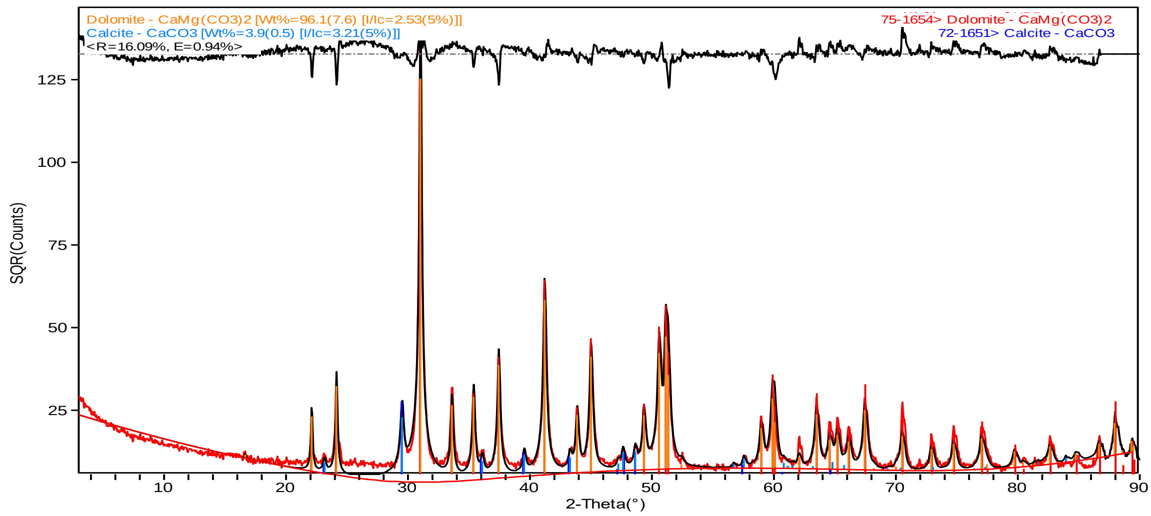

Figure 1 - XRD spectrum of Thasos WMP

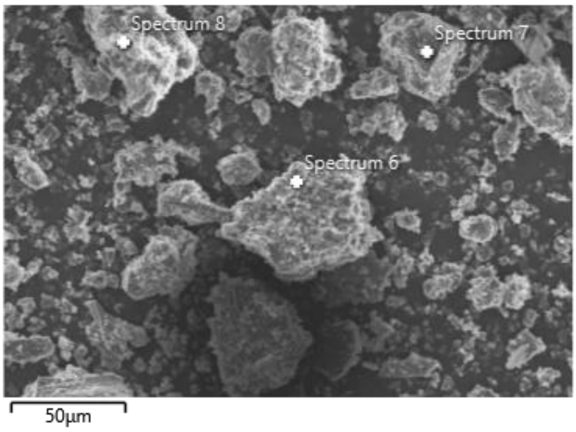

Figure 2 - SEM image of unprocessed Thasos WMP

Table 1 – Elemental analysis of Thasos WMP

Spectrum Label	Weight %		
	Spectrum 6	Spectrum 7	Spectrum 8
O	29	0	62
Mg	12	20	14
Ca	59	80	24
Total	100	100	100

With regard to the characterization of the polymer composites, the use of WMP as an additive did not result in downgrading of thermal, mechanical, and thermomechanical properties of the polymers. These promising results support the potential of utilizing WMP as additives in engineering polymers, minimizing the economic loses of marble industry and preventing environmental pollution.

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