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Abstract

The problem of the large amounts of waste products deriving from ornamental stone industrial activities affects not only the environmental impact but also the resources maintenance and the problem of waste management. This paper presents the essential features of an environmentally attractive reuse of what is currently considered a marble waste: marble sludge, recovered from marble sawing and slurry processing. A research is currently carried out in order to join this by-product with possible industrial applications. Simplified rubber formulations, filled with dewatered marble sludge and cross-linked by vulcanization, have been investigated with the objective of making a comparison with tyre compound obtained by using commercial calcium carbonate filler. From this, rigorous analyses have been carried out. The structural effect of calcium carbonate particles on tyre mixtures tensile strength, hardness, rheometric and morphological properties was inspected. The investigation focused on the materials collected by Orosei marble producing area (NE Sardinia - Italy) and it was carried out in cooperation with the Research & Development Laboratory by Marangoni Spa (Italy). The data emerging from the tests demonstrate how environmental burdens in conjunction with stone production could be reduced to much lower levels, by identifying the way to use marble sludge as filler in high added value products.

Keywords	calcium carbonate filler; marble waste; marble sludge; tyre; environmental impact; dimension stone.
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Highlights

- Waste with possible industrial applications having high added value;
- Feasibility for use of marble sludge as a filler material, instead of commercial CaCO₃;
- Environmentally attractive reuse of marble waste in tyre mixtures production.

WIARBLE SLUDGE





Calcium Carbonate Filler

Comparison between calcium carbonate filler and marble sludge recovered from two wastewater treatment plants

Summary table of results of laboratory testing on MCC					
MCC1	MCC2	МСС3			
2.700	2.719	2.661			
0.136	0.132	0.104			
41.86	43.82	43.94			
2.7	2.7	2.6			
154.9	38.72	54.21			
	MCC1 2.700 0.136 41.86 2.7 154.9	Actory testing on MCC MCC1 MCC2 2.700 2.719 0.136 0.132 41.86 43.82 2.7 2.7 154.9 38.72			



INDUSTRIAL APPLICATION

Tyre Mixture with Marble Sludge







FEASIBILITY OF WARBLE SLUDGE REUSE





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Abstract

The problem of the large amounts of waste products deriving from ornamental stone industrial activities affects not only the environmental impact but also the resources maintenance and the problem of waste management. This paper presents the essential features of an environmentally attractive reuse of what is currently considered a marble waste: marble sludge, recovered from marble sawing and slurry processing. A research is currently carried out in order to join this byproduct with possible industrial applications. Simplified rubber formulations, filled with dewatered marble sludge and cross-linked by vulcanization, have been investigated with the objective of making a comparison with tyre compound obtained by using commercial calcium carbonate filler. From this, rigorous analyses have been carried out. The structural effect of calcium carbonate particles on tyre mixtures tensile strength, hardness, rheometric and morphological properties was inspected. The investigation focused on the materials collected by Orosei marble producing area (NE Sardinia - Italy) and it was carried out in cooperation with the Research & Development Laboratory by Marangoni Spa (Italy). The data emerging from the tests demonstrate how environmental burdens in conjunction with stone production could be reduced to much lower levels, by identifying the way to use marble sludge as filler in high added value products.

Keywords: calcium carbonate filler; marble waste; marble sludge; tyre; environmental impact; dimension stone.

Nomenclature

[MS]: marble sludge

[MCC]: marble calcium carbonate

[MCC1]: commercial micronized CaCO₃

[MCC2]: dehydrated marble sludge deriving from S.I.M.G. s.r.l. company

[MCC3]: dehydrated marble sludge deriving from IN.PRO.MAR. s.r.l. company

1. Introduction

One of the main environmental impacts during the quarrying of dimension stone is represented by the waste material that can reach a great amount, often more than the processed or commercialized one [1].

The way waste is generated offers a differentiation between waste deriving from quarries and waste or offcut deriving from processing plants [2]. More precisely, there are two types of natural stone processing waste: solid (i.e.: unshaped blocks, rubble, crushed slabs/strips/tiles) and semi-liquid or slurry [3] which are mainly composed by stone sawdust and water. These kind of scraps are regarded as an inert waste and usually they are placed in a landfill; furthermore, the main objective of a waste management system is to allow an environmentally and economically advantageous way to sustain the ever increasing volume of waste products.

To avoid the increase amount of waste it is necessary to find alternative ways such as reuse or recycling.

Moreover, the disposal of marble waste, currently represents an additional economic burden for dimension stones companies [2, 4]. State of the art in recovery and utilization of calcareous sawdust mainly relates to its use as a substitute for more expensive ingredient in the building sector [5]. André et al., 2014 [6] and Marras et al., 2010b [7], have reported the feasibility in adding marble industry waste in concrete admixtures, while Topçu et al., 2009 [8] and Felekoğlu, 2007 [9] in self compacting concrete and Gencel et al., 2012 [10] in concrete paving blocks. Applications in red ceramic have been investigated by Devant et al., 2011 [11], Montero et al., 2009a [12] and Montero et al., 2009b [13]. Some studies have been carried out in brick ceramic field [14; 15]. Further investigation has regarded porcelain stoneware [16] and artificial stone slab [17].

However, marble waste use in the building sector has two main disadvantages: low added value (relative to the high market value of micronized CaCO₃) and an insufficient sale, due to the current recession of the building sector. The usage of marble sludge [MS] with high grade of CaCO₃ has not yet become an economically feasible option, to this end, its use should be encouraged in those products which have a higher added value [18, 19, 20].

Calcium carbonate is the most commonly used filler in manufacturing and processing industries.

The aim of this paper is therefore the study of the reuses/recycling options of MS produced by the companies operating in the Orosei Marble quarrying area in tyre compounds in order to replace the commercial micronized CaCO₃, currently acquired by the rubber industries, and produced by milling marble or limestone.

The plastic industry uses inorganic fillers and modifiers, mostly based on calcium carbonate, to be able to offer better features. CaCO₃ is one of the important inorganic powders and is widely used as filler in paints, plastics, and in the rubber industry [21, 22]. In order to satisfy the requirements for its practical applications, it has been widely accepted that elastomeric polymer materials always need to be compounded with nanosized reinforcing fillers [23] which can endow their excellent physical and mechanical properties, such as thermal stability [24], flame retardancy, barrier resistance, stiffness, tensile strength, tear strength, crack resistance, fatigue resistance, abrasion resistance, and so on [25]. Its regular and controlled crystalline shape and ultrafine particle size, together with its hydrophobic surface coating are combined with the benefit for both rubber processing and subsequent physical strength and are of no practical use [27, 28]. The addition of impermeable CaCO₃ particles in different compounds reduces light gas and vapor permeability [26]. Such ingredients as mineral fillers, plasticizers, processing oils, and other specific chemical agents are added not only to modify the tensile characteristics but also to facilitate processing or simply to reduce compounding costs [29].

2. Materials

Three types of marble calcium carbonate [MCC] were used, as CaCO₃ filler, in this research. The first one is the commercial micronized CaCO₃ [MCC1], the second and the third ones are the dehydrated MS deriving from treatment plants, respectively from S.I.M.G. s.r.l. [MCC2] and IN.PRO.MAR. s.r.l. [MCC3]. These companies are currently operating in stone-processing in the Orosei Marble district [30]. Each MS sample was collected at the end of the filter-press sections. MCC1 was provided by a company which produces and sells micronized calcium carbonate from natural sources located in Carrara (Italy). The two processing plants adopt different technologies: the first plan is equipped with gangsaws, slab polishing machines and resin coating installation for slabs, while the second one is equipped with block cutters and tile polishing machines.

During this study the combination of the following components were tested: MCC, SMR10 (CV60), CIIR (EXXON HT1066), N 660, STEARIC ACID, ZnO, MBTS 80%, and VULTAC TB7 commonly used in Marangoni SpA laboratory. With the exception for MCC, all the materials are referred to by their sales name.

2.1 MCC characterization

Because the experimental plan aims at studying the effect of the substitution of MCC1 with MCC2 or MCC3 on the properties of tires compounds, physical, mineralogical and chemical determinations were carried out in order to characterize the three materials. Doing this, it is possible to carry out a comparison between the two MCC supplied and the one which is traditionally used in the tyre production process (MCC1).

Representative samples of MCC1 MCC2 and MCC3 were provided to be submitted to the following tests in accordance with the methodology proposed by Marras et al., 2017 [31].

Grain size analysis was conducted on the samples using a *Sedigraph 5100 Analyser*. Bulk densities were determined using an AccuPyc 1330 V2.01 gas pycnometer manufactured by Micromeritics Instruments. A summary of the obtained data are reported in Table 6.

Lithium metaborate fusion is the technique used for the preparation of the fused sample materials for chemical analysis, which provides suitable solutions for relatively rapid analysis protocols [32]. The chemical solutions were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) manufactured by Varian (710-ES).

The loss on ignition (LOI) was determined by weighing 3 g of test material into a crucible, heating slowly from room temperature to 1000 °C, maintaining this temperature for 16 hours [33]. After cooling in a dryer for 3 hours, the percentage weight loss was calculated. The data of chemical composition and relative proportions in oxides and loss on ignition are summarized in Table 1.

Components	MCC1 [%]	MCC2 [%]	MCC3 [%]
LOI	41.86	43.82	43.94
CaO	53.66	54.90	54.04
MgO	0.35	0.46	0.47
MnO	0.02	0.005	0.007
SiO ₂	3.40	0.08	< 0.01
Al ₂ O ₃	0.33	0.08	0.04
Fe ₂ O ₃	0.13	0.04	0.03
TiO ₂	0.01	0.005	0.002
P ₂ O ₅	0.003	0.02	0.03
Na ₂ O	0.03	0.02	0.02
K ₂ O	0.03	<0.01	<0.01
ТОТ	99.82	99.43	98.58

Table 1: Major components and LOI

3. Experimental

3.1 Melt mixing and samples preparation

Tyre compounds are generally based on unsaturated polymers that have been strengthened with carbon black and are vulcanized by sulfur system [34]. As previously mentioned, calcium carbonate is utilized as filler in tyre blends.

Every recipe contains a number of components, each having a specific function either in the vulcanization process or end use requirement of the product [35]. Specific amounts of all the ingredients were provided (paragraph 2), based on a total of 139 parts per hundred rubber (PPHR). Each additive used has finite duty to perform either during processing or application of a particular compound [36].

Table 2 shows the tyre prep formula applied in the test.

	SAMPLE CODE			
	KA0613	KA0713	KA0813	
MATERIAL	PPHR	PPHR	PPHR	
SMR10 (CV60)	30	30	30	
CIIR (EXXON HT1066)	70	70	70	
N 660	20	20	20	
STEARIC ACID	1.5	1.5	1.5	
MCC1	10	_	_	

Table 2: Loading level of the three compound formulations

MCC2	_	10	_
MCC3	_	_	10
ZnO	5	5	5
MBTS 80%	2	2	2
VULTAC TB7	0.5	0.5	0.5
Total PPHR	139	139	139

This prep was intentionally simplified in order to focus on the effect of CaCO₃ in mixtures. The specimens produced were then signed as follow: KA0613 (prepared with MCC1), KA0713 (with MCC2) and KA0813 (with MCC3).

Compound mixing was carried out in two stages; during the first stage uncured rubber was mixed with essential additives and reinforcing agent carbon black, but prior to mixing, the natural rubber was premasticated. The mixing was carried out in laboratory size 1.6 Banbury mixer (POMINI FARREL S.p.A). Master-batch (uncured rubber and additives) was mixed at 90 rpm screw speed for 290 seconds and the batches were dumped at 150 °C. In the second stage, 1.04 kg of each master-batches was mixed with the curatives in order to obtain the final batches [37]. The mixing was done in the internal mixer at 90 rpm for 90 seconds and the batches were dumped at 110 °C. The mixing schedule is shown in Fig. 1.

Fig. 1: Mixing Schedule

MASTERBATC	H						
15 s			15 s		130°C		150°C
polymers		carb	on black				
chemicals	40 <i>s</i>			120 s		60 <i>s</i>	
FINAL							
15 s		100°C		110°C			
masterbatch							
curatives	40 s		30 s				

The formulated compounds were mixed on a laboratory two-roll mill according to the standard procedure. During mixture, procedure time and cutting operation have been checked. The temperature range for mixing was 70 °C to 75 °C. After final mixing, the compounds are sheeted out at the required thickness (30 mm) and they were prepared for test specimens preparation.

A single sample for each mixture was allocated for the subsequent tests in order to obtain rheological data. The remaining samples underwent the molded stamp vulcanization [38] and then went through mechanical, physical and morphological determinations [39, 40].

3.2 Tyre mixture characterization

Cure features, such as hardness, tensile strength, elongation at break were assessed, according to standard methods ASTM D5289 [41], ASTM D2240 [42] and ASTM D1414 [43].

The cure characteristics of the rubber compounds were determined using MDR-2000 (Alpha Moving Die Rheometer, UK) as per ASTM D5289. The disk-shaped compounds were cut by a cutter 200R manufactured by Flexsys, with a test specimen volume of 4.8 cm³.

When compounded rubber is placed in the rheometer at a temperature which may result in vulcanization, this reaction produces an increase in torque. The rheometer measures cure under nearly true isothermal conditions varying temperature from room temperature to 160 °C in thirty minutes cycle. The chosen temperature is justified by the fact that such temperature is typically used in technology applications [41].

The rheological properties, such as the start of vulcanization scorch time (ts2), optimum curing time (t90), minimum torque (M_L), and maximum torque (M_H) for KA0613 KA0713 KA0813 respectively are shown in Table 3, and for the sake of clarity, curves of real torque against time at vulcanization temperatures of 160 °C are shown in Fig. 2.

Test Parameter	KA0613	KA0713	KA0813
ts2 [min]	7:19	7:45	7:54
t90[min]	10:37	9:59	10:02
M _L [N m] 0.1141		0.1164	0.1254
M _H [N m]	0.4567	0.4418	0.4485
tM _L [min]	0:36	0:38	0:39

Table 3: Parameters for rheological properties

[ts2: scorch time; t90: optimum curing time, M_L : least torque; M_H : maximum torque; tM_L : time for reaching least

torque]





Fig. 2: Rheometric curves: a) KA0613; b) KA0713; c) KA0813.

Once the rubber compositions have reached the desired cure features through the rheological measurements - especially curing speed - eight disk shaped samples were simultaneously cured in a mould for each blend formulation at a pre-selected temperature. The compounds (having different MCC) were molded into 70 mm diameter and 4 mm thick samples and they were cured in an electrically heated press (manufactured by F.lli Sandretto Model: 80-104) where vulcanization took place, at 160 °C for 15 minutes at a pressure of 11-12 MPa, according to the ASTM D3182 [44, 45]. At the end of the curing time, the molded pieces were cooled down at room conditions before testing [46].

3.3 Physical and mechanical tests

After the vulcanization phase the samples were cut as O-Ring [43] in order to carry out the following experimental steps: physical and mechanical tests. The O-Rings had internal dimensions with 56 mm diameter and 4 mm thickness.

Specific gravity test was carried out according to ASTM D792 – Test method A [47], samples prepared as disks, and the volume of each one was more or less 2 cm³. In this test the specimens were weighted in air and then weighted suspended in water.

Samples hardness was determined by the penetration depth of the indenter under the load by means of a Shore-Durometer (manufactured by Zwick) as per ASTM D2240 type A [42]. Minimum thickness of the specimen for the last test is 4 mm. The loading force of Shore A [822 g (1.812 lb)] was applied in three parts of each specimen and the mean values were reported Table 4.

Resilience was determined using Schob Type Rebound Pendulum, according with DIN 53512-2000 [48]. The method specified here serves to determine the resilience of rubber having a Shore A or IRHD hardness of between 30 and 85.

Physical data were listed in Table 4.

Specimen	Specific gravity	Hardness	Resilience	
Unit	g cm ⁻³	Shore A	%	
KA0613	1.088	37	22	
KA0713	1.086	39	22	
KA0813	1.086	39	22	

Table 4: Physical data of the compounds

The tensile stress–strain values were measured as per ASTM D412 "test method B – Cut Ring Specimens" [49]. Tests were carried out on an Zwick/Roell Materials Testing Machine, model Z010, at room temperature and crosshead speed of 500 mm min⁻¹.

Specific gravity, thickness, hardness and elastic yield were previously measured and fed to the computer. See Table 5 for tensile strength test data.

Test Parameter	Unit	KA0613	KA0713	KA0813
EB _%	%	710	728	696
EB	N mm	57,282.48	59,199.55	51,367.74
MOD 0.5	MPa	0.412	0.406	0.402
MOD 1	MPa	0.654	0.641	0.636
MOD 3	MPa	2.036	2.004	1.986
BL	MPa	9.418	9.615	8.543
Tensile strength	MPa	9.373	9.553	8.447

Table 5: Tensile tests data

[EB: elongation at break; MOD 0.5: 50 % Tensile Modulus; MOD 1: 100 % Tensile Modulus; MOD 3: 300 % Tensile Modulus; BL: Breaking Load]

Dispersion of CaCO₃ in polymeric matrices was investigated by scanning electron microscopy (SEM) on a ZEISS microscope (model ZEISS EVO LS15) with 15 kV voltage acceleration.

In order to analyze the non-conductive material samples, gold sputter was applied, so an ultra-

thin coating of electrically-conducting metal (Au) was applied onto specimen.

The micrographs were taken from the coated surface and analyzed with backscattered electron beam detector. A selection of images are reported in Fig. 3.



Fig. 3: SEM micrographs of KA0613 - KA0713 - KA0813

4. Results and discussion

The MCC characterization was carried out by determining the levels of $CaCO_3$ required by the rubber industry as well as by the tyre segment. The following summary table shows these specifications and the values obtained in the laboratory characterization phase.

Table 6: Summary table of results of laboratory testing on MCC according with UNI 8409 [50]

PARAMETER	Unit	MCC1	MCC2	MCC3
Specific gravity	g cm ⁻³	2.700	2.719	2.661
Loss in mass at 105 °C	%	0.136	0.132	0.104
Loss on ignition	%	41.86	43.82	43.94
Fineness: residue at 40 microns	%	2.7	2.7	2.6
Manganese	ppm	154.9	38.72	54.21

As deduced from the above table all the obtained values are acceptable and equivalent.

A comparison of the simplified grain size distribution curves (Fig. 4) shows that the particles are very fine and the grain size distribution is similar for all the samples.



Fig. 4: Grain size distribution comparison

The detected trace elements are contained in negligible amounts and their value is not relevant to the use of calcium carbonate as a filler for the production of tires, the absence of pollutants (hazardous elements and heavy metals) was ascertained. Different metals, particularly transition metals, are characterized as poison with respect to rubber. Within the tyre industry worldwide, a strict specification is maintained to restrict transition metals, specifically copper, iron, manganese, chromium, lead, and cadmium, present in different raw materials [51]. It's important noticed that the manganese is one of the most negative element. In Table 2 is clearly manifested that the manganese content is much more appropriate for MCC2 and MCC3.

The adherence of the tested materials was first checked and compared with industry specifications, and then the impact of MS on the blend features was investigated and compared with conventional composite.

The formulation recipe is indicated in Table 2, while Fig. 1 shows the adopted mixing schedule. The recipes reveal the same compositions, merely varying in $CaCO_3$ quality and not in its amount.

The first assessment has been to ascertain that the workability was good for all compounds during mixing and mastication.

The subsequent vulcanization phase is necessary to transform the raw elastomer to a useful material by providing crosslinks between the long chains of the polymer molecules [52], these compound properties were analyzed by rheometer; in fact, an indirect approach to evaluate the vulcanization level of blends is through the rheometer curves. In this case, the formation of the elastically active crosslinks can be inferred once they are being produced, because a change is

taking place in the torque versus time curves [53]. From the rheometer tests shown in Fig. 2 it can be seen a higher reactivity of MCC2 and MCC3 with respect to MCC1, that is, samples reach the maximum torque at a lower time than at a conventional time. The t90 values are time corresponding to 90% curing, these result is considered the optimum vulcanization time. After the maximum torque has been reached the degradation of the compound can be measured: the reversion is an indication of the resistance of the compound at high temperature and can be useful for the design of the transformation process. It is observed that the cure characteristics of control compound don't change, in an evident way, when the different MCC are filled, so the curing is time depending (Fig. 5).



Fig. 5: Rheometric curves comparison (Torque vs. Time) [KA0613: red - KA0713: black - KA0813: yellow]

At the same time of rheometric studies, a tyre mixture characterization was carried out on pressvulcanized specimens both for physical and mechanical properties.

As seen from the results, the specific gravity for all batches is very similar. The obtained data were listed in Table 4. It is of interest to observe that hardness of rubber is 37 Shore A for KA0613 and 39 Shore A for KA0713 and KA0813 (Table 4). The hardness is increased as the MCC substituted in the polymer matrix. The increase in hardness suggests that the resistance to

indentation is more when MCC2 and MCC3 are filled in the rubber polymer matrix, even when the service life of a batch is not changed dramatically by a slight difference in hardness.

The tensile behavior, such as tensile strength and elongation at break, was examined. Table 5 shows that the tensile strengths of compounds are 9.373 - 9.553 and 8.447 MPa and the modulus at 100% elongation are 0.654 - 0.641 and 0.636 MPa, respectively for KA0613 - KA0713 and KA0813. The maximum elongation at break was reached by the compound KA0713 and the value is 728%. Maximum decrease in elongation at break is observed for KA0813. Elongation at break shows that the compound becomes more brittle when MCC3 is added, in fact the tensile failure elongation at break of 696% is the lowest between the three values.

The difference between the values obtained for the compounds KA0713 and KA0813 could be due to the fact that the sludge resulting from the processing plants that have different production lines, thus, the cause for this reduction in strength and elongation needs to be supported by further investigation.

To summarize, KA0713 has a good elongation at break, this suggests that it can be utilized for the required applications, in fact also a small increase in this parameter is a positive consequence.

Final determination has regarded the filler distribution in the rubber matrix. The characteristics of filler which determine the properties of elastomer compound are: particle size, particle shape and surface area. Filler must make intimate contact with the elastomer chains in order to reinforce the elastomer compound. Therefore, fillers that have a smaller particles have more contact area available and a higher reinforcement potential. The shape of particles also

influences a reinforcement ability of a filler. A planar particles have more surfaces available for contacting the elastomer matrix than spherical particles with similar particle size. They thus have more surface area available to make strong connection with the elastomer. Analyzing the SEM pictures of specimens surface, in Fig. 3, it is clearly seen that the dispersion of filler in the matrix is similar and good for all the compounds.

5. Conclusion

In this research, after MCC characterization, the development of tyre mixtures with the incorporation of MCC as a filler material has been discussed for comparative study. In particular, the role of this filler on the modification of tyre blending properties has been mentioned.

The characterization phase carried out on the MCC has shown:

- MCC produced in the Orosei district respects the specifications required to CaCO₃ in rubber industry and in the specific tyre sector.
- The absence of pollutants shows that the reuse of MS is suitable for commercial purposes.
- Despite the samples come from different plants does not change the characteristics of the final products. These two types of production lines are the most common stone-processing plants in the marble industry.

After the characterization of MCC the real experimental phase has been carried out in tyre sector. The trials made from the research show that all the tyre compounds have very similar

properties. The tests conducted on the specimens have confirmed that the dewatered sludge along with the other traditional constituents has resulted in improvement some qualities of tyre mixture. The manganese content is lower for MS than for MCC1 and whereas the manganese for tires is regarded as a "poison" is a really good point to keep in consideration. Furthermore, mechanical properties, morphological studies using SEM, rheological and physical determinations have made known improvement in performance properties of rubber compounds, indeed it was possible to detect an increase in the elongation at break for the blends obtained by MCC2 as filler.

For all these reasons, waste can be considered as a product with high added value that can be applied in this industrial field. The comparison between analyzed MCC1 and MCC2/MCC3 leads to underline that the MS may be regarded as a good available marketed product.

From comprehensive consideration, the waste taken into consideration may have a potential profit and may be re-used with an environmental added value. It follows that this specific use provides a valuable solution of what would otherwise be a waste material.

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