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Evaluation of Filling Methods Applied to Some Marbles from Diyarbakir Region of Turkey

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In this study, performance of the filling methods polyester, epoxy and ultraviolet resins applied to two different types of limestone were analyzed. The limestone (sedimentary) used originates from two different types of marble that are widely produced and processed in the Diyarbakir region. The effects of the filling methods on loss of material that occurred during the processing stage and the total process costs were also determined.

Key Words: Dimer marble, Filling, Crack, Pore, Epoxy, Polyester, Ultraviolet, Resin.

INTRODUCTION

Natural stones are widely used in buildings, offices and shopping centers as structural elements and as decorational materials. Natural stones are widely preferred to synthetic materials due to their hygienic characteristics. In addition to this, there are major increases in natural stone production.

Because of the natural movements during the genesis period, cracks and pores occur on the structure of the rock mass. During the processing period cracks cause loss of material, consequently increasing cost. Pores decrease commercial value and demand for stone. Besides, this type of structural fault causes the stone to collect dirt and harmful materials. Therefore, as well as losing colour they result in unhygienic surroundings.

Nowadays, thin marble slabs are preferred for reducing static loads especially on high buildings, but cracks and pores in the natural structure of the stone causes difficulties for thin cutting and breakages occur during the polishing and transportation stages.

In recent years, many different types of filling (strengthening) methods are used for obtaining thin slabs from porous and cracked rock masses for regaining them to economy. The importance of strengthening methods are recognized especially when the limited availability of natural stone reserves

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are considered. For this reason, some chemical materials (adhesives) were developed for filling natural stones. By using these chemicals, strengthening of porous, cracked and low resistant marbles become commercially valuable[1]. Nowadays, it is possible to apply filling methods to all kinds of natural stones (including igneous, metamorphic and sedimentary origin stone). Epoxy resins, polyester resins and ultraviolet resins, mastics, cement and surface production products are widely used for different purposes in the natural stone sector as expressed below[2,3]:

• Epoxy resins are used for filling micro pores and making the surface smooth as well as strengthening natural stone slabs, reducing water permeability and increasing gloss after polishing.

• Polyester resins are used for filling pores and cracks that form gaps on natural stones surfaces. They are cheaper and their curing periods are shorter than with epoxy resins.

• Mastics are designed for the aim of filling, retouching and sticking. They can be used both coloured and uncoloured. They become tough quickly so the stone can be ready for polishing within 7-10 min after the filling application.

• Cement filling is especially used for filling pores that cause unaesthetic appearance on travertine.

• UV resins are preferred for accelerating production period. The materials can be transformed and stored just after the filling application.

• Surface protection products are used for increasing the value of polishing and also for protecting the material from external effects, making the material impermeable to water and oil.

The types of stone and the faults of stone have an important effect on the decision of filling methods to be used. If the material has capillary cracks and high breakage ratio, epoxy resin will be preferred because of its high fluidity. On the other hand, polyester resin is preferred for stones which are not breakable but porous structured.

The application surface must be free from dust and oil to allow deep penetration of the stone. Also the clay that settles in the cracks and pores on the stone must be cleared by using water jets and wire brushes. Drying of the stone is the most important process in resin application because all resins except cement are petroleum based. If there is little moisture remaining in the cracks, it prevents epoxy penetration into the cracks. Even if it flows into the cracks, moisture prevents it from penetrating the cracks. So, the resin can be dislocated from the surface of the stone after the polishing stage. Attention must be given to the proportion of the hardener and resin used with polyester resin and epoxy resin. If the stone includes capillary cracks and micro pores, low viscosity resin must be preferred. But if there is a big hole that passes through the other side of the slab, high saturated mastics must be preferred.

Sometimes two or more filling methods must be used together at the same time for eliminating faults on stones. For example, mastic can be used for filling big pores and after that the filling process can be continued by using resins. By decreasing the amount of resin it is possible to reduce the cost. One repair or filling method doesn't inhibit the use of the other. So, it is possible to utilize all the chemical products' advantages[4].

Filling methods were applied to two different types of limestone originating from marbles produced in the Diyarbakir region. The observations recorded and the effects of these methods on the physical and the mechanical characteristics of the marbles are presented in present work. The effects of the filling methods on cost and material loss are also investigated.

EXPERIMENTAL

The application of epoxy resin, polyester resin and UV resin were carried out in the Dimer Marble Processing Plant in Diyarbakir Organized Industry Area on Orient Pink and Tigre Beige marble groups. These marbles are highly demanded in the international market. Chemical analyses of the physical and mechanical characteristics of Orient Pink and Tigre Beige samples used in the laboratory tests are given in Tables 1 and 2.

TABLE-1
CHEMICAL ANALYSES OF MARBLE SAMPLES

Sample	SiO_2 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Al_2O_3 (%)	$CaCO_3$ (%)	$MgCO_3$ (%)
Orient Pink[5]	1.20	0.45	52.55	2.20	-	-	-
Tigre Beige[6]	2.88	1.90	-	-	1.80	91.73	1.30

TABLE-2
PHYSICAL AND MECHANICAL CHARACTERISTICS OF MARBLE SAMPLES[5]

	Orient Pink	Tigre Beige
Hardness (mohs)	4.00	3.00
Unit volume weight (g/cm²)	2.70	2.66
Porosity (%)	0.70	1.51
Water absorption by weight (%)	0.20	0.57
Single axis compressive strength (kg/cm²)	1019.00	1482.70
Strength after freezing (kgf/cm²)	1019.00	-
Strength to bending (kgf/cm²)	170.00	-
Fullness ratio (%)	99.30	-

First, 30 × 30 × 2 cm dimension homogeneous slabs were obtained from both marble types for determining and comparing the efficiency of filling methods which were applied in the plant. Three marble samples per group were prepared as raw material, filled with epoxy resin, polyester resin and UV resin.

For epoxy resin application, the samples which became wet during cutting stage were dried in ovens. Then transparent epoxy resin (main material) was mixed with hardener in determined ratios (80 g resin-20 g hardener) and applied to the stone surface with the use of a spatula until the stone surface filled the cracks completely. Then the slabs were taken by vacuum and samples were kept in natural factory conditions 1 d in summer and 2 d in winter. Each stone was wrapped with nylon. Samples were given to the polishing line after complete polymerization (becoming hard) of epoxy resin.

Before the polyester resin application, the porous samples were calibrated and prepolished for making the pores visible and preventing dislocation of filling material. Then samples were dried completely and components were mixed in determined ratios (2 % hardener to resin). The samples were placed in polymerization ovens to harden, so there is no need to wait. Then the samples were given to the polishing machine.

Finally, UV resin application was made on raw samples. Then, they were given to the polishing line without delay because of the characteristics of the UV filling material.

RESULTS AND DISCUSSION

Performance evaluations: For determining the effects of applied polyester resin, epoxy resin and UV resin filling methods on physical and mechanical characteristics of marble samples, dry unit volume weight, water absorption, compressive strength and seismic velocity tests were carried out on raw and filled Orient Pink and Tigre Beige samples in the laboratory. The results of the tests are given in Table-3.

TABLE-3
RESULTS OF MECHANICAL AND PHYSICAL TESTS OF MARBLE SAMPLES

Sample	Filling situation	Dry unit volume weight (g/cm^2)	Water absorption ratio (%)	Compressive strength (kg/cm^2)	Seismic velocity (m/sn)
Orient Pink	Raw	2.630 ± 0.05	2.43 ± 0.23	452 ± 8.79	3740 ± 18.02
	Epoxy	2.680 ± 0.18	2.28 ± 0.16	465 ± 10.72	3672 ± 31.04
	Polyester	2.731 ± 0.16	2.12 ± 0.15	478 ± 15.71	3644 ± 16.09
	Ultraviolet	2.670 ± 0.27	2.37 ± 0.32	459 ± 8.41	3684 ± 25.23
Tigre Beige	Raw	2.623 ± 0.37	3.47 ± 024	483 ± 16.05	3646 ± 15.13
	Epoxy	2.429 ± 0.35	3.62 ± 0.52	443 ± 9.43	3701 ± 15.71
	Polyester	2.592 ± 0.41	3.84 ± 0.25	472 ± 19.37	3695 ± 26.15
	Ultraviolet	2.339 ± 0.28	4.15 ± 0.29	366 ± 14.86	3754 ± 24.06

At the end of the laboratory tests, it was stated that dry unit volume weights of the Orient Pink samples increased by 1.90 % with epoxy resin filling, 3.84 % with polyester resin filling, 1.52 % with UV resin filling compared to raw samples.

On Tigre Beige marble samples, it was determined that dry unit volume weights were lower by 7.40 % with epoxy resin filling, 1.18 % with polyester resin filling and 10.82 % with UV resin filling as compared to the raw samples.

After the pores and cracks of Orient Pink marble, samples were full of filling materials, their dry unit volume weights had increased. But, the dry unit volume weights of Tigre Beige samples decreased because of the filling materials' expanding effects on pores.

Water absorption tests were carried out on samples for explaining the effects of filling processes on dry unit volume weights. It was stated that water absorption capacities were decreased by 6.17 % with epoxy resin filling, 12.75 % with polyester resin filling and 2.47 % with UV resin filling compared to the raw samples. Moreover, it was seen that water absorption values increased by 4.32 % with epoxy resin filling, 3.84 % with polyester resin filling and 19.60 % with UV resin filling compared to raw samples. It was stated that water absorption decreased on Orient Pink samples because of the deep penetration of filling materials to the structural pores. This was contrary to the effect on the Tigre Beige samples whereby existing structural pores became engaged and expanded by the filling process resulting in water absorption ratios being decreased.

The compressive strengths of samples were evaluated by the help of flexural strength. At the end of the tests, it was determined that compressive strengths of Orient Pink samples were 2.88 % higher with epoxy resin, 5.75 % higher with polyester resin and 1.55 % higher with UV resin than the raw samples. It was observed that all filling methods reduced compressive strengths of Tigre Beige samples. While this descent rate was 8.28 % after epoxy resin filling, it was 2.28 % after polyester resin application compared to raw samples. UV resin filling reduced the compressive strength of applied samples by 24.22 %.

Finally, seismic velocities of marble samples were measured. Seismic velocities of Orient Pink samples were lower by 1.81 % after epoxy filling, 2.57 % after polyester filling, 1.50 % after UV filling than raw samples.

The difference of seismic velocities of Tigre Beige marble samples were 1.50 % higher after epoxy resin application, 1.34 % higher after polyester resin application, 2.96 % higher following UV resin application.

Cost analyses: In addition to the advantageous effects of the filling methods like reducing loss of material, increasing polishing quality and appearance recovery, there is a disadvantage in terms of generating additional cost. The first parameter that affects the cost of the filling process is investment. Maintenance-repair, energy, filling materials and labour are the other factors that affect the cost of filling. Application lines of epoxy resin, polyester resin and UV resin were shown in Fig. 1 and unit cost analyses are given in Table-4.

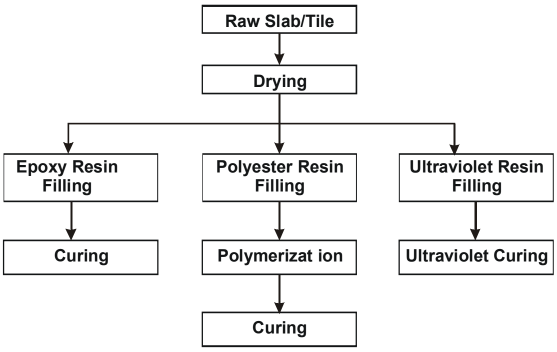

Fig. 1. Flow diagram of filling methods

TABLE-4
COST ANALYSIS OF FILLING METHODS[7]

Filling type	Investment cost of application line ($/m^2)	Maintenance-repair ($/m^2)	Energy ($/m^2)	Labour ($/m^2)	Resin ($/m^2)		Total ($/m^2)	
					Pore	Crack	Pore	Crack
Epoxy resin	Resin line with gas oven = 0.02	0.030	0.25	0.5	1.25	1.25	2.05	2.05
Polyester resin	Resin line with gas ovens = 0.02	0.030	0.25	0.5	1.75	0.50	2.55	1.30
UV resin	UV resin line = 0.036	0.054	0.30	0.5	2.75	1.50	3.64	2.39

Particularly in natural stones which have capillary cracks in their structure, the filling methods applied in the polishing line provides an important economic gain by reducing the breakage rate of stones. The results of the observations made on 100 m^2 Orient Pink samples are shown in Table-5.

TABLE-5
EFFECT OF EPOXY RESIN FILLING ON NET PROFIT OF ORIENT PINK SAMPLES

	Feed amount (m^2)	Filling cost* ($/m^2)	Loss of material (m^2)	Output amount (m^2)	Selling price ($/m^2)	Total income ($)	Extra profit ($/m^2)
Raw	100	-	20	80	25	2000	-
Filled	100	2.05	4	96	25	2400	1.95

*Resin, energy, labour and depreciation are included.

The filling operation on porous natural stones, rather than reducing the breakage ratio, improves the appearance of the stone and increases the unit selling price. The economic gain as a result of polyester application on 100 m^2 Tigre Beige samples is shown in Table-6.

TABLE-6
EFFECT OF POLYESTER RESIN FILLING ON NET PROFIT OF TIGRE BEIGE SAMPLES

	Unit cost ($/$m^2$)
Raw material	14.00
Filled material	20.00
Unit filling	2.55
Net profit after polyester filling	3.45

Conclusion

The results obtained from the study with regard to the performance of epoxy, polyester and UV filling methods applied to Tigre Beige and Orient Pink marbles that are produced in Diyarbakir Region are summarized as follows:

• Generally after filling the pores on marbles with a different material, it is presumed to increase the dry unit volume weight. After the experiments, the results obtained were in line with this view for the Orient Pink samples, but it was the opposite for Tigre Beige sample results.

• The cause of this difference was considered to be due to the structural pores becoming engaged and expanding by the filling process.

• Water absorption of the samples changed in line with the dry unit volume weights.

• Compressive strength values changed in all samples in line with dry unit volume weights.

• After the filling process, the results of seismic velocity experiments were not in line with the obtained results from dry unit volume weight, water absorption and compressive strength experiments. To determine the cause of this difference, further comprehensive studies must be undertaken on different structured marble samples.

• Economically, polyester resin application on porous marbles is more suitable.

• Epoxy resins reduce breakage ratio because of their deep penetration into cracks.

• UV resins are expensive. So, this cost difference reflects on the selling price. But, when the production period is considered UV resins are better than other filling methods due to the acceleration of the production period.

• Physical and mechanical tests for determining the efficiency of filling methods must be selected carefully. The parameters which are effective on slab behaviours (like cohesion, filling resin strength and density) must be considered.

• It was stated that the extra costs incurred by the filling processes were low in comparison to their contributions to the natural stones' marketing value.

• The physical characteristics (pore, crack) and chemical structure of the natural stone, application style of the filling and the chemical content of the filling material must be considered prior to the selection of the filling methods.

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