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PREPARATION OF ARTIFICIAL ORNAMENTAL STONE FROM IRAQI RAW MATERIALS

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ABSTRACT

Artificial ornamental stone is actually a composite material, prepared by mixing polymeric materials with various stones such as sand, crushed dolomite and ground gypsum. This study aims to evaluate local geological raw materials and determine their properties and mineral contents as fillers with polymeric materials. Like the commercial industrial practices, such products contribute to reducing environmental problems compared to other building materials that need to be burned when preparing. In the present work, the raw materials used are local quartz sand, dolomite, and gypsum which are mixed with unsaturated polystyrene in different proportions, and formed by casting. The molds are treated at 90 °C for one hour to obtain a good cohesion between the granules of fillers and the resin. The results are variable depending on the type of filling. Each material used required an appropriate mixing ratio of polymer based on the grain size of the filling materials and their properties. The appropriate proportions of polymer for dolomite, sand and gypsum samples are 25%, 20% and 30%, respectively. Generally, all raw materials used are considered successful for structure clay non-load-bearing tiles according to the requirement of the American Society for Testing and Materials (ASTM) No.C56-71.

تحضير حجر زينه صناعي من مواد أولية عراقية

ميادة صبحي جودي و ايمان مهدي كاظم

المستخلص

حجر الزينة الصناعي من المواد المركبة ذو أبعاد هندسية يتم تحضيره بخلط المواد البوليمرية مع أحجار مختلفة مثل الرمل والدولومايت المكسر والجبسم المطحون وعلى الأغلب يتم استخدام مخلفات الركام الناتج من تحضير حجر متجانس. يهدف هذا البحث إلى تقييم المواد الخام وتحديد خصائصها كمواد مالئة مع المواد البوليمرية. على غرار الحجر الصناعي التجاري يسهم ذلك في تقليل مشاكل البيئة مقارنة بمواد بناء أخرى تحتاج الى الحرق عند التحضير. لتحضير العينات تم خلط المواد الأولية (رمل الكوارتز والدولومايت والجبسم) مع البولي ستايرين غير المشبع بنسب مختلفة، وشكلت بالصب وتم معالجتها بدرجة حرارة 90 °م لمدة ساعة واحدة للحصول على الترابط الجيد بين الحبيبات والمادة الرابطة وكانت النتائج متغايرة حسب نوع المادة المالئة. بالنسبة لعينات الرمل كانت النسبة المناسبة من البوليمر 20٪ والدولومايت 25٪، والجبس 30٪. بشكل عام، تعتبر جميع المواد الخام المستعملة مطابقة لمتطلبات البلاطات غير الحاملة حسب المواصفات العالمية ASTM No.C56-71.

INTRODUCTION

Artificial stones are relatively recent materials in the market of civil construction, and due to environment and sustainability considerations, the development of materials have been increasing worldwide, which could be used in the construction industries and development of

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the decoration and ornamental stones. This would also contribute to the effort of decreasing the environmental problems associated with the disposal of different waste material (Ribeiro *et al*., 2014).

Artificial stones, often known as engineered stones or composite material, consist essentially of a mixture of carefully graded aggregates mixed with an organic resin (polyesters or epoxy). In the past few years, artificial stones showed a high market value and growing demand, because of their uniform characteristics and good properties. The mix composite material improves properties for durability (good mechanical performance and homogeneity) such as high abrasion resistance and impermeability to water and salts (Adesakin *et al.*, 2013). These products represent an excellent option for the recycling of post-process residue by the natural stone industry. Polyesters are the most used binding material, mainly for economic reasons.

Utilizing locally available resources is a cost effective source of filler material (dolomite, sand and gypsum). Mostly, the aggregate waste resulting from preparing a homogeneous stone of geometric proportions is used. It represents a new environmentally friendly product and with the least energy used. Energy issues are the concerns of the world today, and building energy conservation is one of the most important tasks in energy conservation (Mahmood *et al.*, 2019).

- **Previous Work**

Different materials and method have been used during the last decade to get artificial stone. For example, a number of studies were tried to produce artificial stone by using dolomite as major filler in a polymer resin matrix. However, these studies found that numerous parameters have negative impact on modulus, tensile strength, maximum load tests and hardness, depending on the polymer resin ratio, the pressure applied, and the heat maturation (Adesakin *et al*., 2013). Ribeiro *et al.* (2014) used vacuum and compression processing to produce synthetic ornamental marble of 85 wt. % marble wastes added to the polyester matrix. The composites displayed density and mechanical strength comparable to existing commercial artificial stones; the results showed that the water absorption of the synthetic marble was relatively higher owing to a greater porosity of the polyester matrix.

Other studies, such as Lee *et al.* (2008) and Ribeiro *et al.* (2014) used waste glass, granite and marble stone fragments from stone slab processing as recycled raw materials for manufacture of artificial stone slabs by using vibratory compaction in vacuum environment. They found that higher compaction pressure improves mechanical properties up to the level which compaction pressure promotes the breakdown of the particles. Raw materials are mixed with unsaturated polymer resin as binder under different conditions of compaction pressure, vibration frequency and vacuum conditions, finally the water absorption, density, flexure strength; compressive strength and tensile strength are studied.

Different workers have used epoxy resin as a matrix material for making many composites. For example, Ramakrishna *et al.* (2006), Balakrishna *et al.* (2016), Goncalves *et al.* (2014), and Demartini *et al*. (2018) used granite stone powder as fillers at different mass percentages with various types of epoxy. Hussien and Kadhum (2017) used crushed dolomite rocks with epoxy at different mass percentages; reached up to 70%, to prepare synthetic marble for sanitary ware, which gave higher resistant. It is known that the price of epoxy is higher than polyester, thus, it was suggested to replace it by Polyester Resin (PS) (Ribeiro *et al*., 2003).

- **Materials and Methods**

– Raw materials:

- **Dolomite:** Five kilograms of dolomite, from the Dammam Formation (Al-Khadari site at Al-Salman Village, SW Iraq), is crushed by a jaw crusher, to a particle size of less than 2 mm, then the particle size (1 – 2) mm is selected for the process.

- **Quartz Sand:** Five kilograms of quartz sand from the Rutba Formation (Er Radhuma mine, W Iraq) is sieved to a particle size between (150 – 850) µm,

- **Gypsum:** Two kilograms of gypsum from the Fatha Formation (Zurbatia area, SE Iraq) is ground down to < 106 µm. According to Al-Janabi *et al.* (1993), the samples are analysed using wet analysis method to determine SiO_2, TiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O and Na_2O. To determine the mineralogy of the studied samples, they are analysed by X-ray Diffraction (XRD), after milling to 200µm. The laboratory work of this study is carried out at the laboratories of Iraq Geological Survey, Baghdad.

– **Binder:** Unsaturated polyester resin is used as a binder in this study, which is a synthetic polymer that is a basic component of some types of glue. It is utilized in many different industrially relevant markets, but in general it is used as the matrix material for various types of composites. The properties of liquid product are shown in Table (1).

Polyester resin is cured with the addition curing agent which is commonly used as hardening agent which is called as hardener, Methyl Ethyl Ketone Peroxide (MEKP) in a liquid state (Fahad, 2017). This is added in terms of 1: 10 to the weight of polyester (Girish *et al.*, 2016).

Table 1: Specifications of the unsaturated polyester (Crawford and Thrane, 2002), (cP: centipoise)

Property	Appearance	Density g/ cm^3	Viscosity cP	Acid Number mgKOH/g	Gel time min
Unsaturated polyester	Clear-liquid	1.15	450	30	5

– **Preparation of the artificial ornament stone:** Three sets of experiments were designated to study variable percentages of the raw materials used (dolomite, sand and gypsum in several fractions) as a filler material, to select the required particle size for the desired texture, as shown in Table (2). The selected materials were washed and air-dried before mixing, except gypsum. Then, they were mixed with unsaturated polyester and hardener as binding materials.

The mixture, after stirring, is casted into a plastic mold, which has a shape of cylinder, then let until hardness. The prepared samples were later removed from the mold after 24 h and put in an oven up to 90 °C for 1hr following (Demartini *et al*., 2018) procedure, then set for physical and mechanical properties determination. The block diagram, showing the flow of experimental work, is illustrated in Figure (1).

Table 2: Preparation of artificial stone and mixing proportions

Raw material	Sample No.	Particle size (μm)	Hardener %	Resin %
Sand	S1	150 – 850	10	90:10
	S2		10	85:15
	S3		10	80:20
	S4		10	75:25
Dolomite	D1	1000 – 2000	10	80:20
	D2		10	75:25
	D3		10	70:30
Gypsum	G1	<53	10	75:25
	G2		10	70:30
	G3		10	65:35

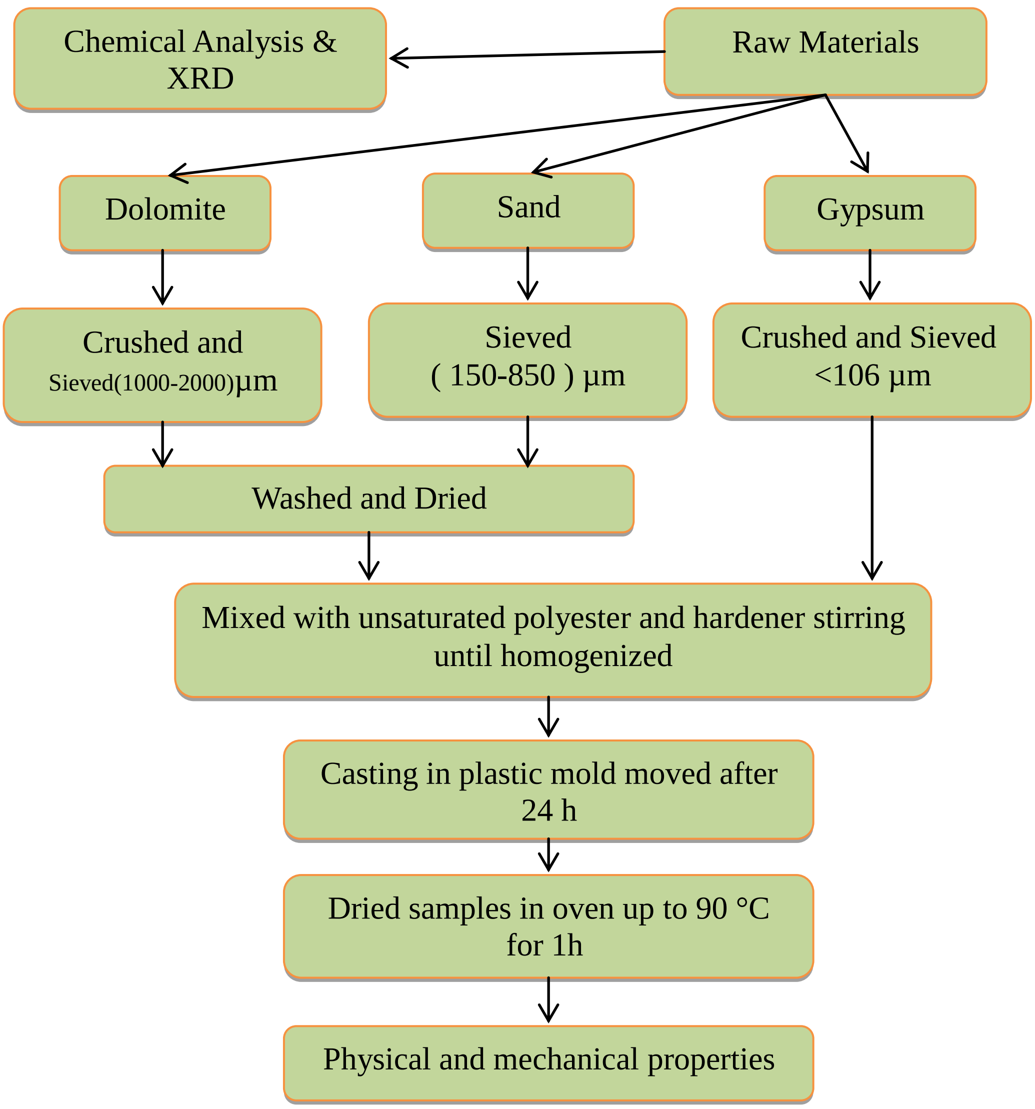

Fig.1: Block diagram of artificial stone preparation

– **Measurement of Physical and Mechanical Properties:** Brick and tile specimens were tested for linear shrinkage, bulk density, compressive strength and tensile rupture strength and water absorption values. They are calculated according to the ASTM C67, 2005, using the following equations (1, 2, 3, 4, 5, 6, 7):

- **Linear Shrinkage (*L sh*):**

$$L\ sh.\% = \frac{Ld - Lf}{Ld} * 100 \ldots\ldots\ldots\ldots\ldots\ldots \textit{Equation 1}$$

Ld = length of the dried specimen in centimeter.
Lf = length of the fired specimen in centimeter.

- **Bulk density:** The bulk density provides a general indication of the product quality.

$$\text{Bulk density} = A/V\ g/cm^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \textit{Equation2}$$

Where:
A: dry weight of the sample that was measured.
V: total volume.

- **Compressive Strength:**

$$S = W/A\ \ N/mm^2 \ldots\ldots\ldots\ldots\ldots\ldots \textit{Equation 3}$$

Where:
S = cold crushing strength (N/mm^2).
W = total maximum load indicated by the test machine (N).
A = average of top and bottom areas of the specimen perpendicular to the line of the application of the load, (mm^2).

- **Modulus of rupture**

$$\text{Modulus of rupture} = 3WL/2bd^2\ \ N/mm^2 \ldots\ldots\ldots\ldots\ldots\ldots \textit{Equation 4}$$

Where:
W = maximum load indicated by the testing machine, in N.
L = distance between the supports in mm.
b = average over-all width, face to face, of the specimen, in mm.
d = average over-all depth, face to face, of the specimen, in mm.

- **Tensile Test (Stress-Strain):** Tensile test is widely used to provide the designer with information about material strength, maximum elongation and other properties. The stress used in such curve is a longitudinal stress in the tested specimen and expressed as:

$$\sigma = P/A\ N/mm^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textit{Equation 5}$$

Where:
σ: longitudinal stress for specimen (MPa).
P: applied load (N).
A: original cross sectional area before testing (m^2).

The strain which is used in such stress-strain curve is a linear strain and can be expressed as:

$$\text{Strain } (\varepsilon) = \frac{\Delta L}{L_\circ} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \textit{Equation 6}$$

L : final length (m). $\Delta L = L - L_\circ$
$L_\circ$: original length (m).

From the tensile curve, Tensile strength (MPa) can be calculated as:

Tensile test = σ/ε MPa …………………… *Equation 7*

RESULTS AND DISCUSSION

- **Characterization of starting materials**

The results of chemical and mineralogical analyses of dolomite, sand and gypsum materials used in this investigation are shown in Table (3) and Figures (2, 3 and 4), respectively. They are considered from the raw materials of high purity. The reason for using different types of raw materials is to observe the effect of different characteristics to prepare artificial stone. The chemical analysis results show the chemical composition of the natural raw materials which are used as fillers with resin to prepare the artificial stone. The choice of unsaturated polyester resin for this study is related to its low cost and easy process ability for general purposes (Mansour *et al*., 2017).

The materials used are of high purity and have been adopted being the most appropriate and strongest except gypsum. It is a well known fact that the hardness of quartz sand and dolomite is higher than gypsum. Different sizes have been adopted for the filling materials as in the dolomite, quartz sand and gypsum to obtain ornamental stones with a rough, medium and soft texture as shown in Fig.5.

Table 3: Chemical analysis of the raw materials
(LOI: Loss on ignition, w.o.c.: Water of crystallization)

Comp. %	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	CaO %	MgO %	LOI %	SO_3 %	K_2O %	Na_2O %	TiO_2 %	w.o.c %
Dolomite	1.27	0.18	0.35	30.94	20.20	46.40	0.63	0.07	0.08	<0.01	-
Quartz Sand	98.86	0.08	0.31	0.13	<0.02	0.31	<0.02	0.02	0..02	0.024	-
Gypsum	0.84	0.20	0.38	31.58	0.24	21.05	44.97	-	-	0.03	19.37

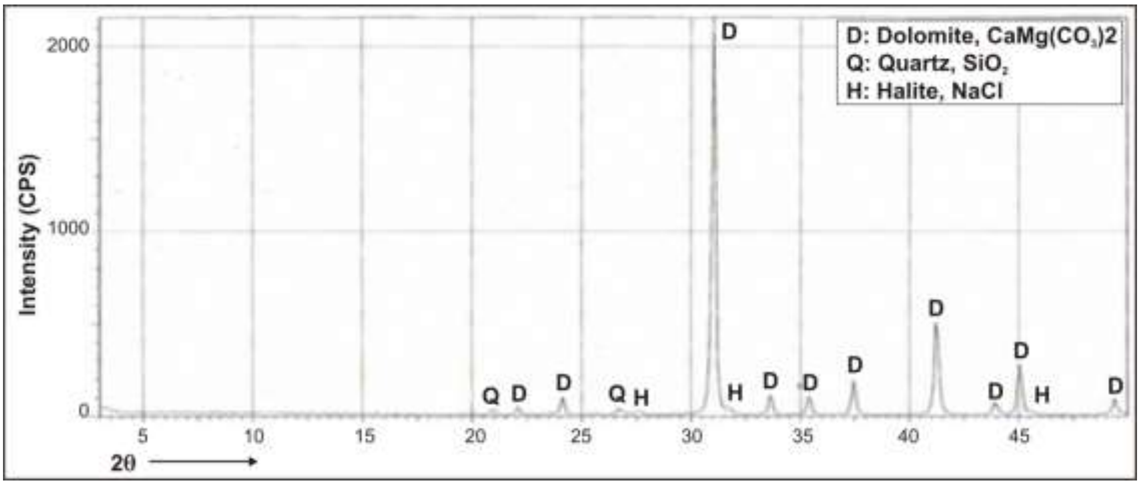

Fig.2: XRD pattern of dolomite

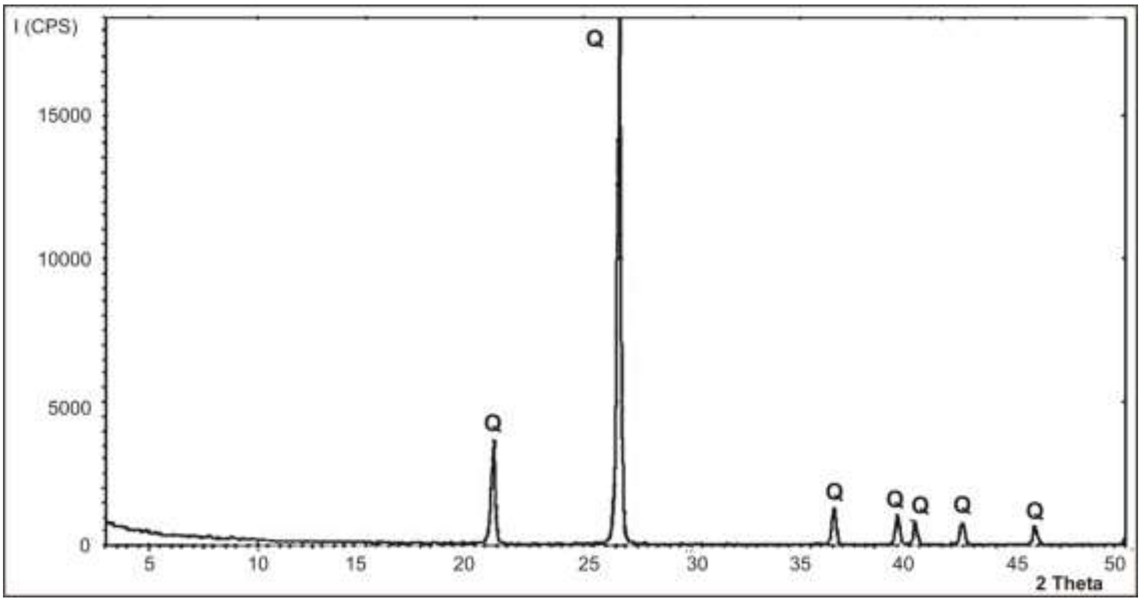

Fig.3: XRD pattern of Er Radhuma quartz sand

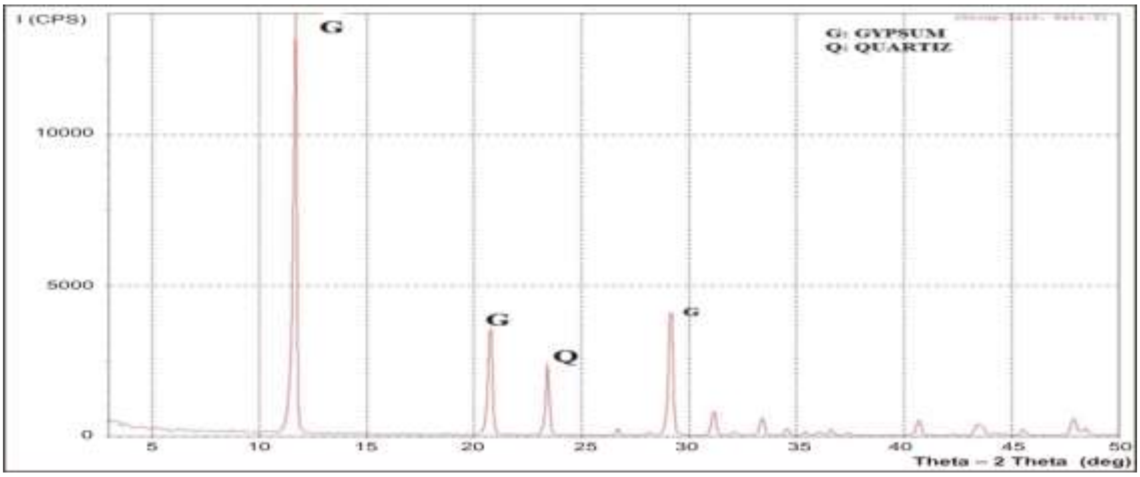

Fig.4: XRD pattern of gypsum

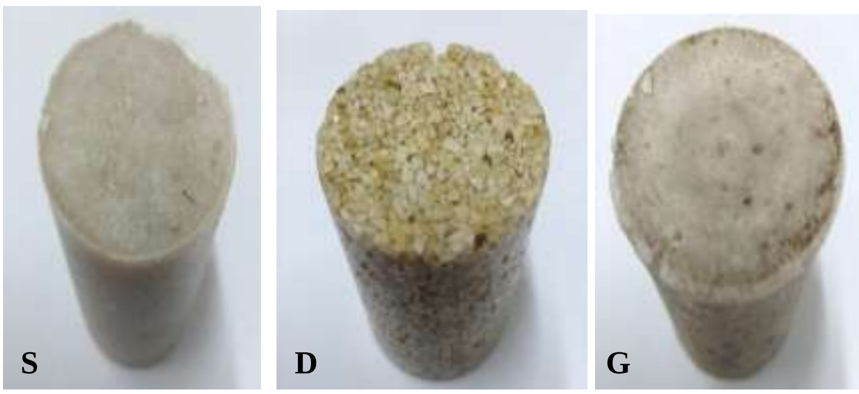

Fig.5: Samples of artificial stone (S, D, G)

- **Physical and Mechanical Properties of Artificial Stone**

The properties of artificial stone are determined to show the stability of the products after manufacture, as well as the efficiency of the mixing proportions and type of the ingredients used to prepare the artificial stone (different percentages of raw materials and binders).

The physical and mechanical properties of artificial stone are shown in Tables (4, 5 and 6), respectively where the most important tests for assuring the engineering quality of veneer materials are illustrated. The physical and mechanical properties of the materials are proportional to the percentage of unsaturated polyester resin mixed (Reis, 2011). It is observed that there is a variation in the relative density values when changing the filling material (quartz sand, dolomite or gypsum), but generally the highest density is obtained when using the proportion of resin up to 25% for each sample separately. These results are due to the behavior of the resin materials and their efficiency of penetration into the interfaces of the grains, which leads to an increase in density Figure (6). As for water absorption, a significant decrease in the rate of water absorption was observed for all samples Figure (7). This is due to the action of the resin in closing the external pores when increasing the resin up to > 20%.

Concerning the compressive strength test (Tables 4, 5 and 6) the highest compressive strength is achieved, when using quartz sand or dolomite particles as fillers and mixed with 20% polyester resin, As for gypsum samples, the highest resistance is achieved when using 25% of resinous materials (Figure 8). This depends on the homogeneity of the distribution of the bonding material between granules, and the high values refer to the high coherence of the particles (Adesakin, *et al*., 2013).

Tensile strength test is one of the important mechanical properties to determine the rigidity of samples and their resistance to deformation as a result of polymer material presence. As shown in Figure (9), the properties of tensile test, using 30% polystyrene to gypsum gives the maximum slope which indicates an increase in the rigidity and a decrease in ductility. The specimens become stiffer with the increase in filler content (Balakrishna *et al*., 2016), this is important in determining the highest permissible mixing ratio. Tensile strength is a maximum value of strength in the stress- strain curve drawing with PS % (Figure 10), which gave 7.75 MPa when mixing with 30% polystyrene. This determined the successful ratio with less deformation match to Figure (9).

Table 4: Physical and mechanical properties of quartz sand-based samples

Sample No.	Quartz Sand: Resin %	Bulk density gm/cm^3	Comp. strength N/mm^2	Water absorption Cold water 24 hr.%
S1	90:10	1.75	20.78	9.4
S2	85:15	1.71	36.00	1.14
S3	80:20	1.82	52.63	0.18
S4	75:25	1.89	22.83	0.15

Table 5: Physical and mechanical properties of gypsum-based samples

Sample No.	Gypsum: Resin %	Bulk density gm/cm^3	Comp. strength N/mm^2	Water absorption Cold water 24 hr.%
G1	75:25	1.78	43.37	0.28
G2	70:30	1.74	32.66	0.29
G3	65:35	1.69	28.13	0.32

Table 6: Physical and mechanical properties of dolomite-based samples

Sample No.	Dolomite: Resin %	Bulk density gm/cm^3	Comp. strength N/mm^2	Water absorption Cold water 24 hr.%
D1	80:20	1.75	45.0	0.15
D2	75:25	1.95	35.09	0.12
D3	75:30	1.80	28.32	0.08

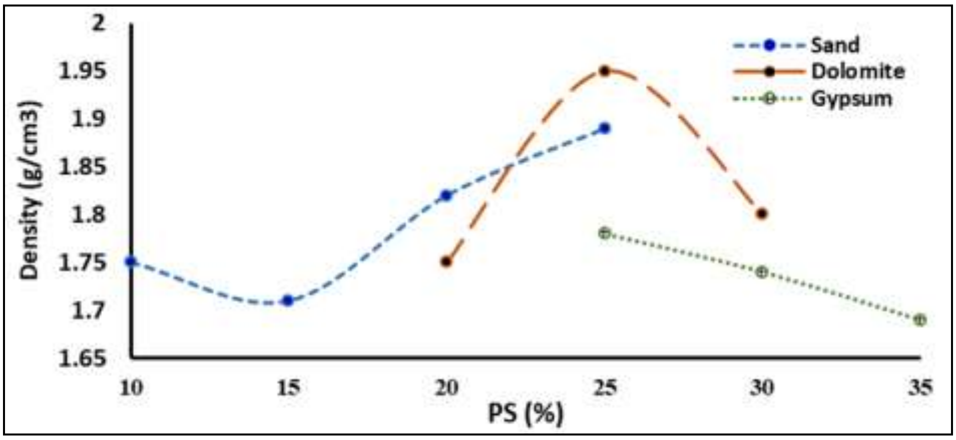

Fig.6: The effect of increasing polyester (PS%) on bulk density of The| prepared artificial stone samples

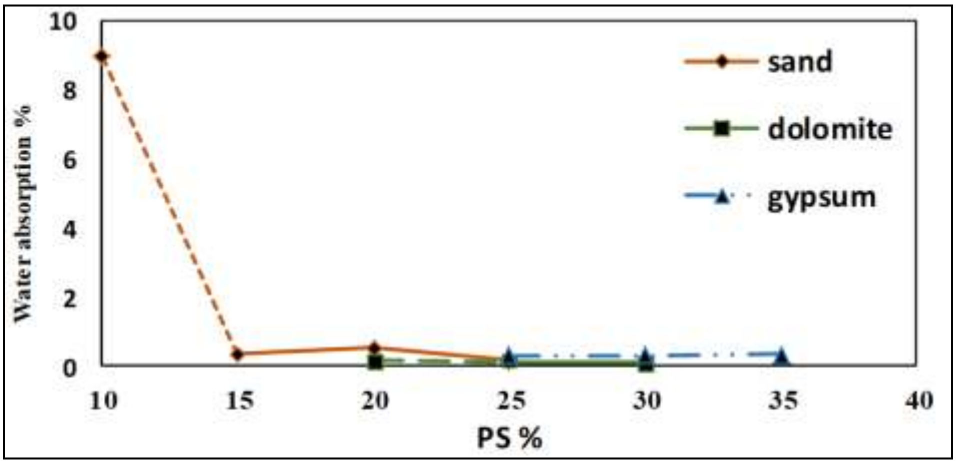

Fig.7: The effect of increasing polyester (PS%) on the water absorption of the prepared artificial stone samples

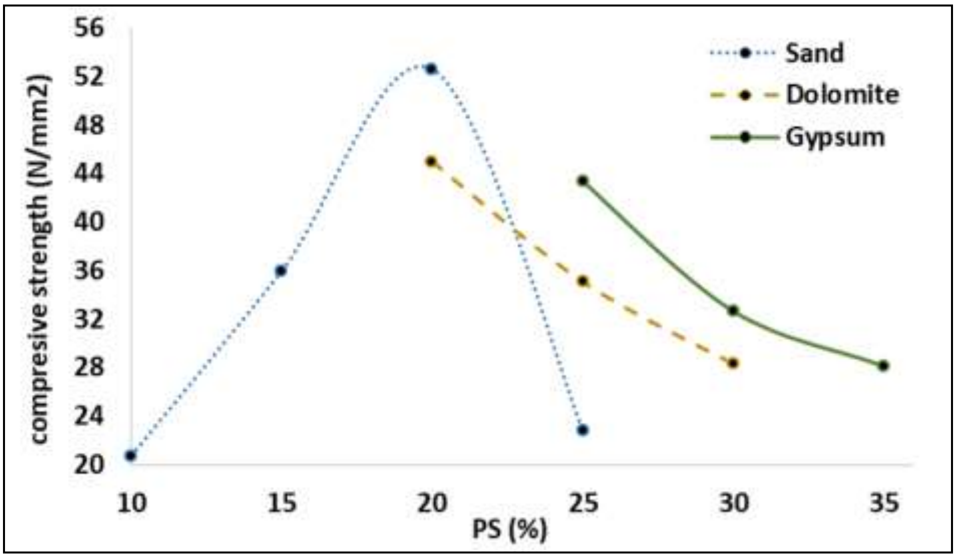

Fig.8: The effect of increasing polyester (PS%) on compresive strength of the prepared artificial stone samples

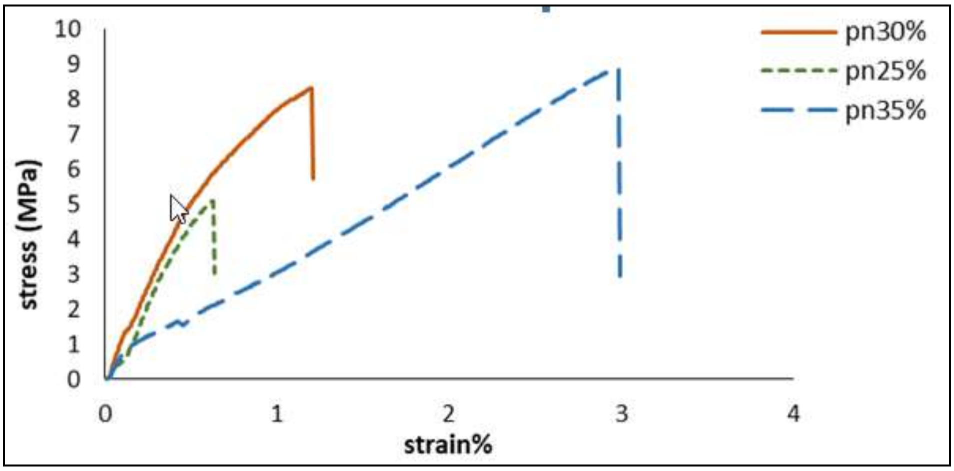

Fig.9: Properties of tensile strength test for the gypsum-based samples

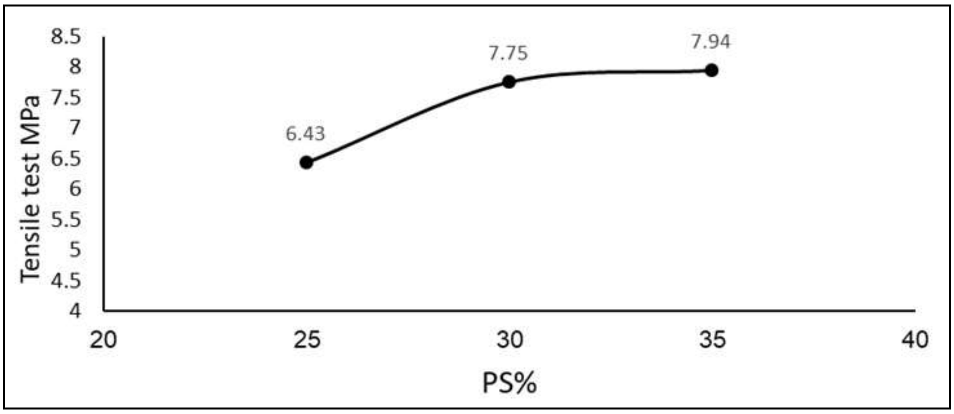

Fig.10: The effect of increasing polyester (PS%) on the tensile stress of the gypsum-based samples

- **Comparison with natural limestone**

The physical and mechanical properties of the artificial stone are compared with the commercial natural limestone. The natural raw materials show lower compressive strength of (20.38 N/mm^2) and higher water absorption of (2.86%), compared with the artificial stone as shown in the present results (Tables 4, 5 and 6). The better properties of the artificial stones are achieved by the interconnection force and close pores between natural grains with polymer material (Adesakin *et al*., 2013).

The specification of Iraqi standard for dimension limestone No.1387 specify the compressive strength by >12 N/mm^2 and water absorption not greater than 12%. The disadvantage of the natural stone above ground is caused by weathering interaction over time that leads to higher water absorption and color change. On the other hand, the reasonable interfacial adherence between the filling materials and the polyester matrix in the artificial ornamental stone explains their competitive physical and mechanical properties developed in this work. Therefore, all samples are suitable according to the requirements of (ASTM C56, 2013; and ASTM C34, 2003).

CONCLUSIONS

- Quartz sand, dolomite and gypsum from local Iraqi deposits represent, after sizing and impregnation with polystyrene resin, suitable basic raw materials for the manufacturing of artificial ornamental stones with acceptable mechanical and physical properties,
- The best polystyrene proportions obtained from the tests are 20, 25, and 30% for the quartz sand-, dolomite- and gypsum-based samples respectively. The increase or decrease of the resin materials above or below these values for all samples result in the failure of the samples in terms of physical and mechanical properties.
- According to the results achieved in this work, the prepared artificial stones can be used as ornamental stone and building units.

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