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Characteristics of Micro and Nano Composite from Marble and Granite Wastes

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Abstract: In this work, New composite material was developed from marble and granite waste , the unit for recycling of marble and granite wastes was designed, the prototype was tested in manufacturing of thermoplastic based composite from marble and granite wastes respectively, the main characteristics of both composite materials were measured, the structure of the new composite materials were determined by SEM, the composition were determined by EDX analysis, the particle size and elemental analysis were evaluated by the same technique, the volume resistivity and abrasive wear was evaluated. Thermogravimetric Analysis (TGA) was measured to determine the operation temperature of the new composite materials. Thermal conductivity of new composite material was calculated from the role of mixture. The main applications of the new composite materials were mentioned according to the characteristics measured.

Keywords: nano composite, granite, marble, waste recycling, characteristics

1 Introduction

Recycling waste as useful material is a very important environmental management tool for achieving sustainable development [1]. On the other hand, recycling waste without properly based scientific research and development can result in environmental problems greater than the waste itself [2],[3]. The successful research and development of a new building material or component using waste as raw material, is a very complex and multi-disciplinary task having technical, environmental, financial, marketing, legal and social aspects. Now the cost of construction materials is increasing incrementally [4],[5]. For example, the cost of cement during 1995 was Rs.1.25/kg and in 2008 the price increased ~ three times. In case of bricks the price was 0.66 per brick in 1995 and the present rate is Rs.2.5 per brick [6],[7]. Similarly, over a period of 10 years from the year 1995 the price of 147 sand has increased four times [8]. Also due to high transportation costs of these raw materials, demand, environmental restrictions, it is essential to find functional substitutes for conventional building materials in the construction industry [9],[10]. Growth of population, increasing urbanization, rising standards of living due to technological innovations have contributed to an increase both in the quantity and variety of solid wastes generated by industrial, mining, domestic and agricultural activities [11],[12]. About 6 million tons of wastes from marble industries are being released from marble cutting, polishing, processing and grinding. The granite and marble dust is usually possesses a major environmental concern [13]. In dry season, the granite and marble powder or dust dangles in the air, flies and deposits on vegetation and crop. All these significantly affect the environment and local ecosystems. The granite and marble dust disposed in the river-bed and around the production facilities causes reduction in porosity and permeability of the topsoil and results in water logging. Further, fine particles result in poor fertility of the soil due to increase in alkalinity [14],[15]. Use of industrial wastes and by products as an aggregate or raw material is of great practical significance developing building material components as substitutes for materials and providing an alternative or supplementary materials to the housing industry in a cost effective manner and the conservation of natural resources[15].Microsoft word has been used widely in writing scientific papers, LaTeX also has been widely used to generate a PDF and offers flexibility, very organized equations and elegant styles [1].

2 Experimental Sections

2.1 Materials

The matrix is polymethyl metha acrylate (PMMA. It is

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thermoplastic prepared from monomer (methyl methacrylate) by additional polymerization process; polymer was in the granule form with 5mm diameter.

Filler (Marble Wastes) Marble refuses consists wet refuse (sahla) (wet wastes):

It is a type of the wet refuse where its percentage of water reaches about 70%. It is sticky and it is produced from the processes of leveling and polishing. Commercially it is known as (Al Sahala) or Al Sahla. The sticky refuse is heavy in weight and big in size. This is due to the existence of water in it. but they are very soft granules.

Chemically, they are crystalline rocks composed predominantly of calcite, dolomite or serpentine minerals. The other minor constituents vary from origin to origin. average chemical composition of marbles, Table (10) shows the chemical composition of marble.

Table 1: The chemical composition of marble.

Compound	Symbol	percent
Lime	(CaO)	28-32%
Silica	(SiO_2)	3-30%
Magnesium oxide	MgO	20 to 25%,
Iron oxides	FeO + Fe_2O_3	1-3%,
losses	Loss On Ignition (LOI)	20-45%

Impurities in Marble the major mineral impurities in marble are Quartz -Tremolite Actinolite -Chert -Garnet -Biotite -Muscovite -Microline -Talc -Fosterite, while the major chemical impurities in marble are SiO_2 -Fe_2O_3 -2Fe_2O_3 -3H_2O-Limonite -Manganese -Al_2O_3 -FeS_2(pyrite).

Filler (granite Wastes) granite refuses consists wet refuse (sahla) (wet wastes):

granite is an igneous rock with at least 20% quartz and up to 65% alkali feldspar by volume. Granite is nearly always massive (lacking any internal structures), hard and tough, and therefore it has gained widespread use throughout human history, and more recently as a construction stone. The average density of granite is between 2.65[2]and 2.75 g/cm^3, its compressive strength usually lies above 200 MPa, and its viscosity near STP is 3–6 • 10^{19} Pa·s.[3]

Melting temperature of dry granite at ambient pressure is or 1215–1260 °C (2219–2300 °F);[4] it is strongly reduced in the presence of water, down to 650 °C at a few kBar pressure.[5]

2.2 Chemical Properties of Granite

Table 2: A worldwide average of the chemical composition of granite, by weight percent, based on standard analyses:[7]

Compound	Symbol	percent
Silica	SiO_2	72.04%
Alumina	Al_2O_3	14.42%
Potassium oxide	K_2O	4.12%
Sodium oxide	Na_2O	3.69%
Lime	CaO	1.82%
Iron oxide	FeO	1.68%
Iron oxide	Fe_2O_3	1.22%
Magnesium oxide	MgO	0.71%
Titanium oxide	TiO_2	0.30%
	P_2O_5	0.12%
Manganese oxide	MnO	0.05%

2.3 Preparation of Material

Grinding

A blinder with variable speeds is used to change the pieces of thermo-plastics into powder form, the blinder speed is about 15,500 rpm, work at 200 volt - 50 Hz, and the grinding time is about 90 sec. Switch off for cooling is lasted about 180 sec to prevent the agglomeration of the particles and achieve reasonable degree of quality in grinding. The retained granules after sieving will be returned to blinder.

Mixing

2.4 Treatment of Marble & Granite Wastes

The wet refuse preparation consists of three consecutive steps: -.

A . Preparation of wet refuse by drying phase, the mixture is automatically pushed to the drying room the heaters are adjusted at 120°C for period from three to four hours, for guaranteeing the drying process. Wet refuse (Sahal) is got out of the dryer in the form of fragile masses which are transferred by a conveyor to the automatic turning over room as it is turned over and made in the form of powder suitable for sifting and mixing.

Mixing & Sieving

The outcome of the two phases is collected in the automatic sieve. Automatic mixing for thermoplastic in the powder form with at different aspects ratio was done. The amount of material required was calculated. The mixture moves to the final drying and mixing phase. This phase is fitted with heaters at 120°C for a period from 3 to 4 hours. This is for guaranteeing the final drying of the two mixtures.

2.5 Manufacturing Process

Plastic powders and treated marble wastes were mixed toge ther in the solid state. The mixture is heated at the required temperature, according to its components. The heating rate depends on the type of the joining material, compression and cooling were done for heated mixture. Nano composite material is fabricated, figure (1) shows the recycling of marble and granite wastes unit, the new composite material is distinguished with the light weight and the ability to endure scratch and damping capacity comparing with the natural marble. It is also liable for the easy formation and is distinctive with different colors and shapes

Fig.1: The recycling of marble and granite wastes unit.

2.6 Measurements & Detection

Scanning Electron Microscope (SEM)

The specimens were examined by scanning electron microscope (SEM) operating at a nominal accelerating voltage of 30kv. Specimen preparation is very simply accomplished by cutting a thin slice of the specimen containing the surface of interest, chemical and electro etching were done at standard conditions, the samples were inserting into the specimen chamber for direct examination of the laser irradiation effects on the structure.

Energy dispersive X-ray "EDX"

The quantitative method of elemental analysis of the samples has been examined at the Chemical labs of the ministry of Telecommunication in Egypt by SEM JSM-T200 at 25KV acceleration voltage, 20mm working distance, and magnification 200x, (1peak omitted 0.02 KeV). Each value is at least an average of 2 readings

2.7 Electrical Measurements

Volume Resistivity

IEC 60093:1980, Method of test for volume resistivity and surface resistivity of solid electrical insulating materials American society for testing and materials-ASTM D257-07 standard test methods for DC resistance or conductance of insulating materials. Figure (2) shows the circuits for volume resistivity measurements

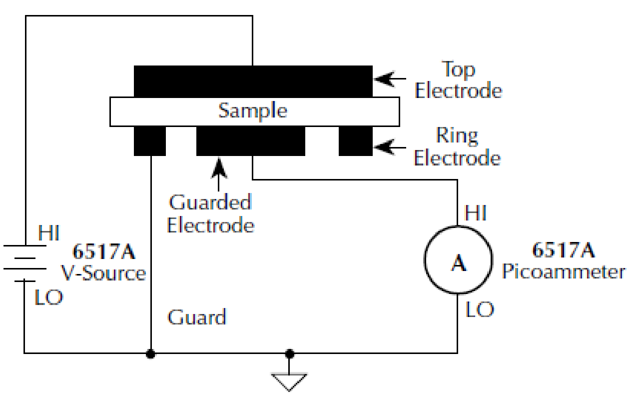


Fig. 2: The circuits for volume resistivity measurements.

$\rho = RA/L$

ρ electrical resistivity

R electrical resistance of uniform material Ω (ohm)

A cross sectional area m2

L specimen length m

2.8 Mechanical Measurements

Abrasive Wear

The Egyptian standard no 269/1 -2005 and The Egyptian standard no 269/2 -2005 for heavy duty services, test conditions are sliding distance 352 cycle, applied pressure 224 gm/cm^2 and the abrasive material is sand quartz. Egyptian standard is compatible with international standard of Abrasion Test according to ISO 9352 or ASTM D 4060. According to the Egyptian standard the limit for normal duty must achieve not more than 6 mm loss in thickness and average loss in thickness is not more than 5.2mm, for heavy duty services the limit is not more than 3.6 mm loss in thickness and average loss in thickness is not more than 3mm.

2.9 Thermogravimetric Analysis (TGA)

Thermogravimetry thermal analysis (TGA) testing - ASTM E1131, ISO 11358, **Thermogravimetric Analysis (TGA)** measures the change in mass of a material as a function of time and temperature. Ideally, it is utilized to assess volatile content, degradation characteristics, thermal stability, aging and lifetime breakdown, and sintering behavior/reaction kinetics.

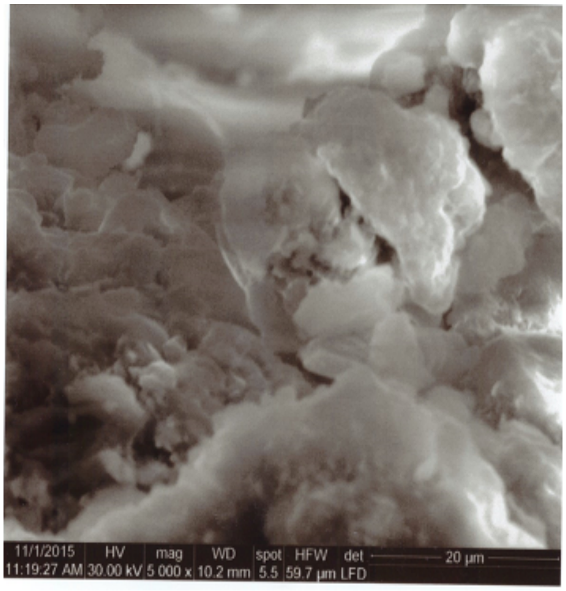
3 Results and Discussion

3.1 SEM (Scanning Electron Microscope)

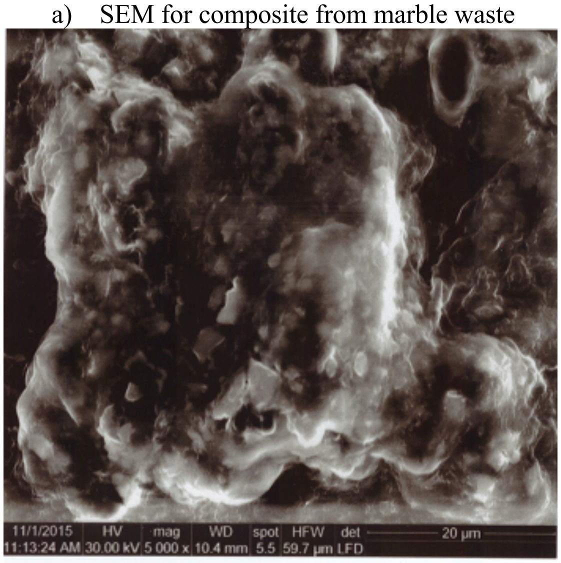
The structure of the new composite material materials from marble and granite wastes at magnification 5000x were evaluated as shown in figure 1 . a) is the structure of the new composite material from marble waste, the average particle size in the sample is ranges from 50µm to 300µm. While b) is the structure of the new composite material from granite waste at the same magnification, the average particle size in the sample is ranges from 150µm to 500µm. the distribution of particles in both samples are semi homogeneous in the micro and nano size.

3.2 Spectroscopic Analysis

The chemical composition was evaluated by spectroscopic analysis techniques. Elemental analysis for composite material from marble waste was shown in table (3), and table (4) shows the elemental analysis of the composite material from granite waste. the distribution of the elements in the two composites were seem to be different, in composite from marbles waste there was some sulfur content about 0.24% while the composite from granite waste was free of sulfur content. The major element in composite from marbles waste is Calcium while silicon is the main element in composite from granite waste. the two composite material have great difference in structure and composition which explain that they have great difference in manufacturing parameters and electrical and mechanical properties.



a) SEM for composite from marble waste



b) SEM for composite from marble waste

Fig. 3: SEM of composite materials from marble & granite wastes at 5000x.

Table 3: Elemental analysis of the composite material from marble waste .

Marble chemical composition	
Element	**Concentration %**
Ca	**10**
Fe	**1.94**
K	**0.26**
Na	**0.79**
Si	**2.51**
Al	**0.54**
S	**0.24**

Table 4: Elemental analysis of the composite material from granite waste.

Granite chemical composition	
Element	**Concentration %**
Ca	**1.18**
Fe	**1.68**
K	**3.93**
Na	**3.53**
Si	**31.58**
Al	**7.12**

Figure 2. shows the EDX analysis distribution of all elements in the composite from marbles wastes, while figure 3. shows the EDX distribution of all elements in the composite from granite wastes

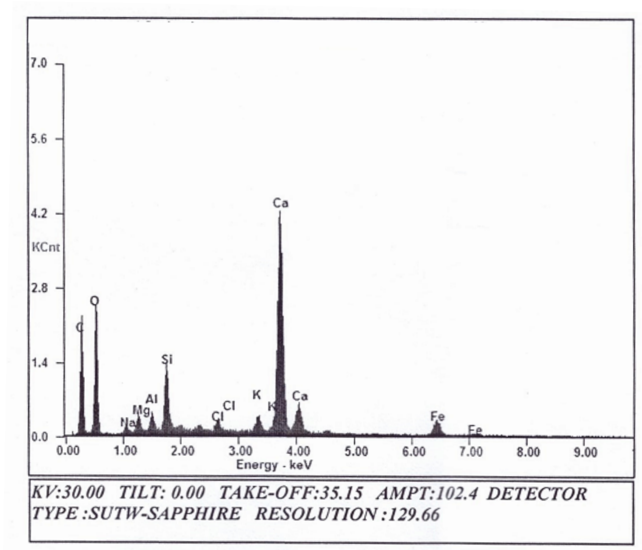


Fig. 4: EDX analysis of the composite materials from marble wastes

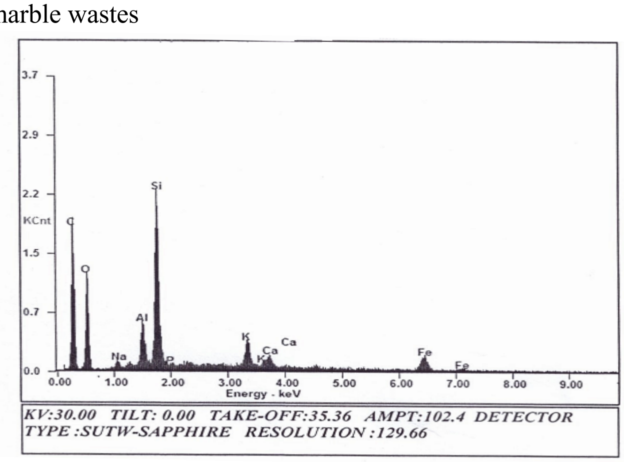


Fig. 5: EDX analysis of the composite materials from granite wastes.

3.3 Electrical Resistance

Volume Resistivity

Electrical resistivity is measure of the ability of the material to flow electrical current, the increase in value of volume resistivity is considered as indication that the structure is free of defects, the electrical resistivity is directly related to the concentration of charge carriers and to their mobility, micro and nano particles from marble and granite wastes work as impurities inside the structure cause a sharp reduction in conductivity , the structure is considered as heterogeneous dielectric material in randomly distributed composite, this structures have sharp rise in electrical resistivity ρ due to scattering of electrons and charge disturbances to the potential field of the lattice, the superior electrical resistance in the material due to micro and nano additives which cause structure and substructure imperfections that prevent vibration of ions, the composite materials are insulated material suitable for different electrical applications. Table 5 shows Volume resistivity of composite material from marble and granite wastes by IEC 60093:1980, Method of test for volume resistivity and surface resistivity of solid electrical insulating materials according to American society for testing and materials-ASTM D257-07 standard test methods for DC resistance or conductance of insulating materials

Table 5: Volume resistivity of composite material from marble and granite wastes.

	volume resistivity	Sample dimension	
		Thickness(cm)	Diameter (cm)
Marble1	>0.66 $*10^{14}$	1	5.3
Marble 2	>1.16 $*10^{14}$	1.9	9.7
Granite	>1*10^{14}	2.20	9.7

3.4 Mechanical Measurements

Abrasive Wear

abrasive wear data were obtained from pin-on-drum tests where the wear path is essentially linear, all tests were carried out in dry ambient air laboratory conditions. According to the Egyptian standard, the sliding distance is 352 cycle under pressure 632 gm/cm$^{2.}$ Abrasive wear rates with different kinds of the reinforcement relative to the abrasive medium, quartz sands abrasive which is substantially harder than either the matrix (PMMA) or the reinforcement (marble and granite) was used. abrasive wear in ductile composites reinforced with a hard second phase is presented based on the salient mechanisms of sliding wear, namely plowing, cracking at the matrix/reinforcement interface or in the reinforcement, and particle removal. In the test beginning during the first cycles under load any portion of reinforcement that is removed as wear debris can contribute to the wear resistance of the material; and work as self-lubricant. The strong bond energy between the matrix and reinforcement plays a significant role in improving the wear resistance at the interface for both composite material from marble waste and granite waste respectively, composite material from marble wastes have superior wear resistance relative to composite from granite although granite reinforcements are harder secondary phase relative to marble, Self-lubrication action is the main reason for these phenomena, during sliding the marble particles are fragmented in the beginning more easily and work as self-lubricant media which prevent more fragmentation. Table 6 shows abrasive wear of composite material from marble and granite wastes

Table 6: Abrasive wear of composite material from marble and granite wastes.

Properties	**Marble**	**Granite**
Sample dimension		
Diameter (cm)	5.34	3.18
Thickness (cm)	1.16	1.07
Weight before (gm)	34	11
Weight after (gm)	33	10.5
Density (gm/cm^3)	1.31	1.30
Thickness loss(mm)	0.34	0.49
Average Thickness loss (mm)	0.34	0.49

from the above table both composite materials from marble (0.34mm loss in thickness) and granite wastes (0.49mm loss in thickness) are suitable for heavy duty and normal duty applications. According to the Egyptian standard the limit for normal duty 6 mm loss in thickness and average loss in thickness is 5.2mm and for heavy duty services 3.6 mm loss in thickness and average loss in thickness is 3mm.

3.5 Thermogravimetric Analysis (TGA)

The TGA curve (below) is labeled in terms of the identity of the components. The sample was heated from room temperature to 900°C at a rate of 5°C/min in air. as shown in the figure (4) and (5), TGA measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, thermal analysis was used for studying reactions in the solid state, weight change sensitivity less than 0.01 mg. Samples was analyzed in the form of small pieces so the interior sample temperature remains close to the measured gas temperature. In practice thermal analysis gives indication about the dimension stability, determines temperature and weight change of decomposition reactions, which often allows quantitative composition analysis. the un-change in weight of the composite materials until 100C°

to 120C °used to determine water content in a material and reactions with air, oxygen, or other reactive gases

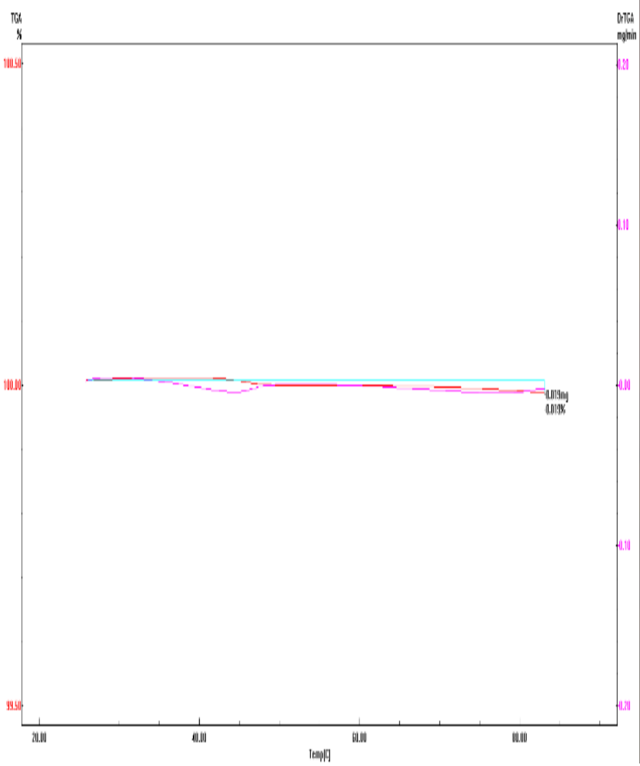


Fig. 6: (TGA) Analysis of composite material from marble waste.

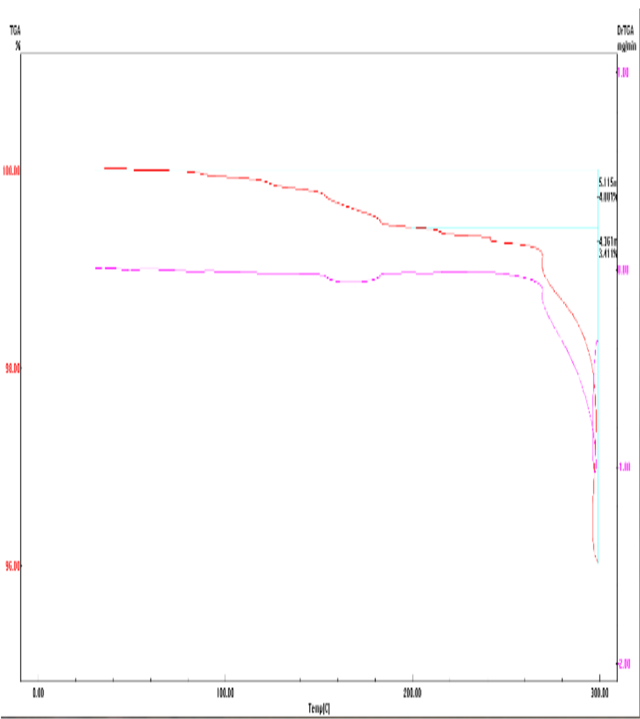


Fig. 7: (TGA) Analysis of composite material from granite waste.

3.6 Thermal Properties

The thermal conductivity of the new composite materials is calculated by role of mixtures, the thermal conductivity of the new composite materials is calculated by role of mixtures, Table 7. shows the thermal conductivity of both matrix and additives at room temperature.

$$V_m K_m + V_f K_f = K_{Composite} \quad (1)$$

K_c thermal conductivity of composite material
K_m thermal conductivity of matrix
K_f thermal conductivity of filler
V_m volume fraction of matrix
V_f volume fraction of filler

Table 7: thermal conductivity of matrix and additives.

Material	**Thermal conductivity [W·m^{-1}·K^{-1}]**	**Temperature [K]**	**Notes**
Acrylic Glass (Plexiglas V045i)	0.17[2]-0.19[2]-0.2[3]	296[2]	
Granite	1.73[48] - 3.98[48]		($72\%SiO_2+14\%Al_2O_3+4\%K_2O$ etc.)
Marble	2.07[48]-2.08[6]-2.94[6][48]	298[6]	Mostly $CaCO_3$

0.17x0.75+ 2.07x0.25= 0.1275+ 0.5175 = 0.645 (**W·m^{-1}·K^{-1}**)
0.2x0.75+ 2.94x0.25= 0.15+0.735 = 0.885 (**W·m^{-1}·K^{-1}**)
Thermal conductivity of composite from marble waste 0.645 to 0.885 (**W·m^{-1}·K^{-1}**) at room temperature
0.17x0.75+1.73x0.25=0.1275+0.4325 = 0.56 (**W·m^{-1}·K^{-1}**)
0.2x0.75+ 3.98x0.25=0.15+0.995 = 1.145 (**W·m^{-1}·K^{-1}**)

Thermal conductivity of composite from granite waste 0.56 to1.145 (**W·m^{-1}·K^{-1}**) at room temperature. The new composite materials are considered as thermal insulated material

4 Conclusions

The new composite material consists of micro and nano particles from marble and granite waste impeded in thermoplastic matrix.
The new randomly distributed composite material is special type of heterogeneous dielectric materials.
The superior electrical resistance in the material due to micro and nano additives which cause structure and

substructure imperfections that prevent vibration of ions, the composite materials are insulated material suitable for different electrical applications.
composite material from marble wastes have superior wear resistance relative to composite from granite although granite reinforcements are harder secondary phase relative to marble, Self-lubrication action is the main reason for these phenomena, during sliding the marble particles are fragmented in the beginning more easily and work as self-lubricant media which prevent more fragmentation.
The new composite is suitable for heavy duty and normal duty wear applications. According to the Egyptian standard
The new composite materials are considered as thermal insulated material with dimension stability until 100C° to 120C.
The unique structure of the new composite materials is resulting from the new manufacturing technique and the manufacturing unit design.
The new composites are economic and suitable for electrical and thermal insulation techniques beside heavy duty tribology applications in summary, we demonstrate why Microsoft Word is useful, the font of main text is 10 Times New Roman with single line spacing of 6 pt after and 0 pt before.

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