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Preparation and characterization of PMMA/stone waste nanocomposites for marmoreal artificial stone industry

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Abstract

The current study concerns the preparation and characterization of marmoreal solid surface materials based on polymethylmethacrylate (PMMA) nanocomposites filled with waste stones of marble, granite and basalt. Hydrophilic nanosilica and clay Halloysite nanotubules (HNTs) were the two types of nanofillers used to prepare PMMA/stone waste nanocomposites. The effect of nanofiller type and stone nature was investigated by Rockwell hardness, flexural strength, impact toughness, abrasion loss, water absorption and luminous transmittance measurements. The prepared artificial stone samples have an eye-catching decorative effect of alabaster when lighted from rear using a low energy light source.

Keywords

PMMA nanocomposites, autoclave polymerization, diffused transmittance

Introduction

Natural stones were extensively used for construction purposes for human civilization due to their unique aesthetical and technical characteristics. Solid wastes of natural stone processing can be classified into various forms such as coarse, fine powder, aggregates, larger stone pieces, cobbles, damaged blocks and slabs.[1,2] The presence of these wastes is considered one of the major environmental problems faced by many countries, not only for its harmful effects on public health but also for tarnishing the face of civilization.[3,4] Common ways of stone wastes treatment are land fill, incineration, chemical recycling and the utilization of energy from combustion.[5] Another useful way to solve the problem of stone waste is their recycling in different forms for industrial activities particularly construction and building materials.[6] Recently, the recycling of stone waste granules (SWG) became an important issue due to their physical properties and suitability for a wide range of applications.[7] This can be done by incorporation of stone wastes via free radical polymerization in polymethylmethacrylate (PMMA) nanocomposites which are excellent bending matrices due to their improved hardness, solvent resistance and glossiness.[8] The fabricated sheets have the properties of artificial stones which can be used for interior and exterior building applications.[9,10]

The study aims to prepare a cheap replacement of natural stones such as marble, basalt and granite which are expensive, hardly processed and enormously heavy when used in building applications. This will be achieved by applying autoclave polymerization to prepare innovative PMMA nanocomposite materials entrapped with SWG. The produced artificial stone composite panels are proposed to have somewhat glossy colored appearance of natural stones in addition to promising mechanical strength and physical properties.

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Experimental techniques

Materials

Methylmethacrylate (MMA) monomer (Merck, Darmstadt, Germany) was freed from inhibitors by distillation at 50°C under reduced pressure (1 mbar) using rotary evaporator (BUCHI ROTAVAPOR R-114, Switzerland). Hydrophilic nanosilica (Aldrich, USA) was used as a thixotropic agent and anticorrosive material, and the particle shape and size were determined by transmission electron microscope and found to have a spherical shape with 7 nm diameter, as shown in Figure1(a). Nanoclay Halloysite nanotubules (HNTs) were purchased from (Aldrich) without any chemical modification, this material has an average tube diameter of 50 nm and inner lumen diameter of 15 nm as determined by the manufacturer (Figure1b).[11] SWG having average maximum diameter of about 5 mm were produced by successive sieving of pulverized natural waste stones such as marble, granite and basalt. The shape and size of SWG were determined by the representative photograph of granite waste presented in Figure 2.

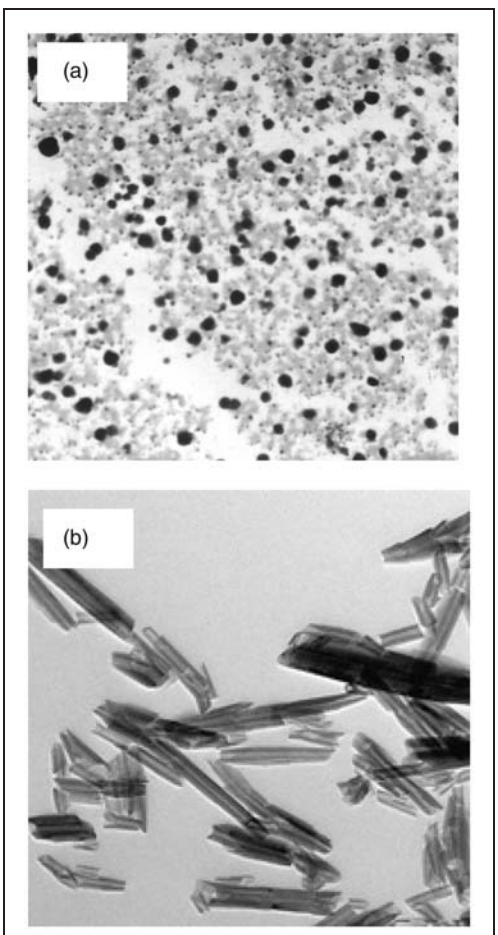

Figure 1. TEM images of (a) hydrophilic nanosilica and (b) halloysite nanotubules characterized by Aldrich Co.[7]

PMMA nanocomposite preparation

The polymer syrup (PMMA-MMA) was prepared by adding 0.1 wt% an azobisisobutyronitrile (AIBN) initiator (DuPont, USA) to MMA, the solution was refluxed at 100°C under reduced pressure (10^{-3} bar) for 1 h to increase the monomer viscosity and subsequently reduce the polymerization time. The viscosity of the resulting syrup was 200 cP determined using a rotational viscometer (BROOK FIELD DV-II, USA). Alumina trihydrate (ATH) (Albemarle Corp., Korea) was added with concentration about 20 wt% as antiflammable and anti-corrosive material.[12] Ethylene glycol dimethacrylate was added as a cross-linking agent with a concentration 0.5%. Afterwards, hydrophilic nanosilica and HNTs were added as received with concentrations of about 2 wt% and 3 wt%, respectively. These concentrations were recorded to give the maximum improvement of thermal stability and mechanical properties for PMMA nanocomposites.[13,14] The measured viscosity of the nanocomposite polymer syrups was 800 cP and 1050 cp for nanosilica and HNTs additives, respectively.

PMMA/SWG nanocomposite preparation

Before preparing artificial stone sheets, the moisture adsorbed on the surface of SWG was removed by heating it in a vacuum drying oven (Yamato Scientific, USA) at 10^{-2} bar and 150°C for 24 h. The selected SWG were soaked in the nanocomposite syrups and left in open air atmosphere to dry at room temperature in order to enhance the product rigidity.[13]

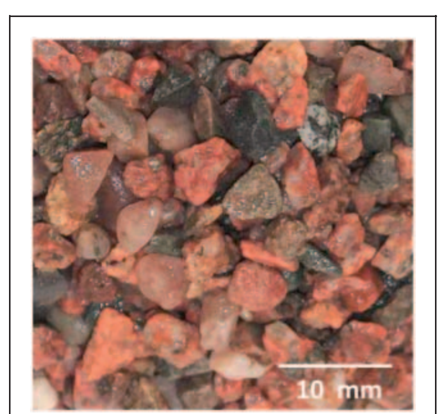

Figure 2. A photo image of granite stone waste.

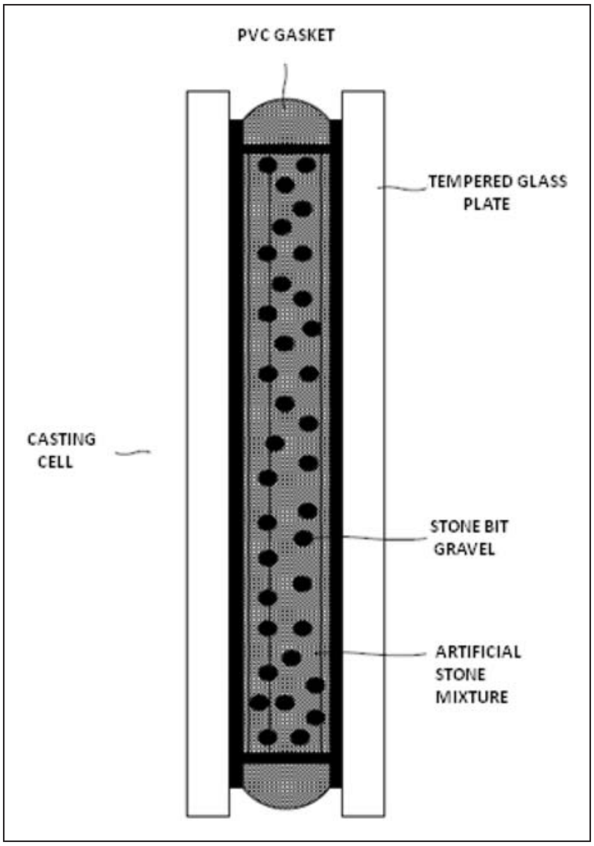

Figure 3. A front side view of the casting cell.

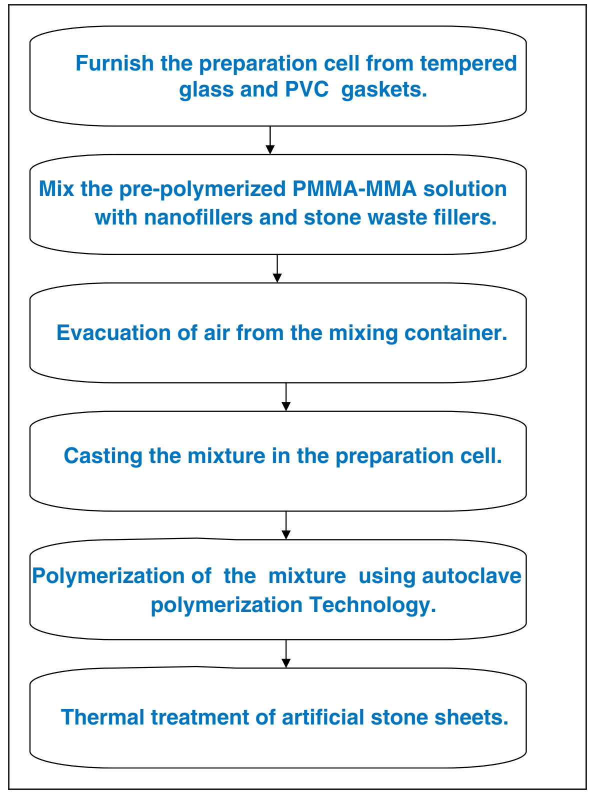

Figure 4. A schematic diagram illustrating the flow of artificial stone production.

The nanocomposite syrups of PMMA/SiO_2 and PMMA/ clay HNTs were mixed with different concentrations of the investigated waste stones. The concentration of SWG to the total weight was changed from 10% to 80% in order to obtain the best mechanical properties accompanied with the lowest product density. The liquefied PMMA/SWG nanocomposites were poured into a rectangular cell made of tempered glass of dimensions $50 \times 50 \times 2\,cm^3$ to form the nanocomposite solid surface material. A detailed description of the casting cell is shown in Figure 3 and the polymerization stages are presented in Figure 4.

Autoclave polymerization technique

In this technique, the casting cells were placed in an autoclave in which the pressure and temperature can be regulated according to the desired thickness of the prepared PMMA/stone nanocomposite. Firstly, the autoclave was evacuated from air and then pressurized at 2 bar in the presence carbon dioxide or nitrogen at 60°C. The temperature and pressure were maintained constant until the polymerization process is completed and then the casting cells were cooled slowly to room temperature while still under pressure in the autoclave. After cooling to the room temperature, the pressure was reduced gradually to the normal atmospheric value, and the casting cells were put in electric oven at 100°C for 2 h for the final curing to attain the complete polymerization of PMMA/SWG nanocomposites.

Testing methods

The mechanical properties were tested using tensile machine (UNIVERSAL Tester AT 2.5KN 84-02, Messmer instruments, UK). A three-point bending test was carried out for the investigated PMMA/SWG nanocomposites in accordance with ASTM standard (D7264) at a strain rate of 1 mm/min.[15] Impact strength measurements have been carried out according to (ASTM D 6110-2) using charpy impact tester (43-02 monitor/impact, Messmer instruments, UK). The hardness of the samples was measured using Rockwell hardness (HRC) testing machine (Wilson 2000T, USA) according to ASTM (E18-11).[16] The abrasion resistance test was performed according to ASTM (D1044–08e1)[17] by using Taber® abrasion tester (Messmer 5130, UK). Water swelling test of PMMA/SWG nanocomposites was examined according to ASTM (D570-98 e1).[18] The luminous transmittance of PMMA/SWG nanocomposites were specified according to ASTM D1003[19] using a Haze meter (NDH 5000, Nippon, Japan).

Results and discussion

Figure 5 shows the surface morphology of artificial stone samples based on PMMA/SiO_2 and PMMA/clay HNTs nanocomposites impregnated with the investigated SWG. It is clear that the samples are homogeneous and have uniform distribution of stone pebbles in the polymer matrix, which in turn leads to the improvement of the mechanical properties. In addition, all the nanocomposites have eye-catching decorative effect specially when lighting from rear by using a low energy light source as shown in Figure 5.

The values of diffuse and parallel luminous transmittance (T_D and $T_{//}$) are listed in Table 1, and it is clear that the total transmission (T) of PMMA/SWG/SiO_2 nanocomposites is higher than that of PMMA/clay HNTs. This can be ascribed to the fact that SiO_2 nanoparticles have high-quality optical properties compared to clay HNTs.[20]

The HRC test is an empirical indentation hardness test that can provide useful information about the engineering materials. This measurement may correlate to tensile strength, abrasion resistance, ductility and other physical characteristics of PMMA/stone nanocomposites.[21] It is also useful in improving the quality of the prepared artificial stone by determining the optimum concentration of SWG impregnated in PMMA nanocomposite matrices. Figure 6 illustrates the effect of SWG concentration on the HRC of PMMA/nanoSiO_2 and PMMA/clay HNTs. It is noted that the hardness is increased by increasing the stone concentration up to a certain value ($C_{max} = 50$ wt%) and then decreases. The decrease of the hardness beyond C_{max} can be ascribed to the decrease of the polymer network connections at higher filling levels.[22] The maximum values of HRC obtained for the prepared artificial stone sheets are listed in Table 2. It is clearly observed that the highest hardness values are obtained for PMMA/stone/clay HNTs due to the mechanical toughness of clay HNTs compared to hydrophilic nanosilica. In addition, it is noted that the hardest PMMA nanocomposites are those impregnated with granite. This can be ascribed to the fact that the hardest mineral in granite (quartz) is harder than the hardest mineral in basalt (feldspar).[23] From this study, it can be affirmed that the optimum concentration for preparing PMMA/SWG nanocomposites for artificial stone applications is 50 wt%.

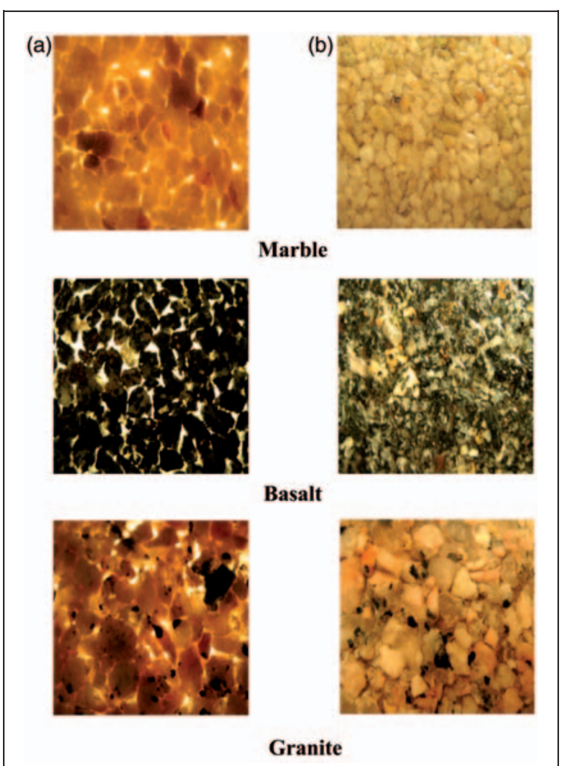

Figure 5. The surface morphology artificial stone samples based on (a) PMMA/SWG/SiO_2 and (b) PMMA/SWG/clay HNTs nanocomposites.

Figure 7 illustrates the flexural stress–strain curves of PMMA/SWG nanocomposites recorded according to ASTM(D 7264) at a strain rate of 1 mm/min. It is noticed that the stress strain curve of pure PMMA changed from hard and brittle to that of hard and strong material. The modulus of elasticity E has been estimated according to Hook's law relation[24]:

$$\sigma = E\varepsilon$$

where σ is the flexural stress, ε is the strain, and E is the modulus of elasticity which is clearly a measure of material resistance to deformation. The values of E, yield maximum stress σ_m, and maximum strain ε_m are listed in Table 3. The tabulated values showed a remarkable improvement in the flexural strength of

Table 1. Luminous transmittance (%) of artificial stone samples based on PMMA/SWG nanocomposites.

	PMMA/SiO_2/SWG			PMMA/clay HNTs/SWG		
Stone	T_D	$T_{//}$	T	T_D	$T_{//}$	T
Marble	45.3	20.1	65.4	7.0	1.1	8.1
Basalt	24.7	23.5	48.2	4.8	0.5	5.3
Granite	30.5	25.6	56.1	5.6	0.8	6.4

artificial stone samples based on clay HNTs than those based on nanosilica. This can be explicated by the fact that PMMA/clay HNTs nanocomposite has higher flexural strength than PMMA/SiO_2 nanocomposite as proved by the calculated values of E, σ_m, and ε_m shown in Table 4. Regarding the effect of stone type on the mechanical performance of PMMA/SWG nanocomposites, the best results were obtained for those filled with granite. This can be attributed to the increased hardness of granite stone and improved adhesion between SWG and PMMA nanocomposites.[25]

The impact strength of artificial stone samples based on PMMA/SWG nanocomposites is recorded in Table 5. It is noticed that the impact resistance is increased from 21 kJ/m^2 for the PMMA/HNTs nanocomposite having marble stone filler to 26.8 kJ/m^2 for the nanocomposite having granite stone filler. This can be due to the excellent compatibility between

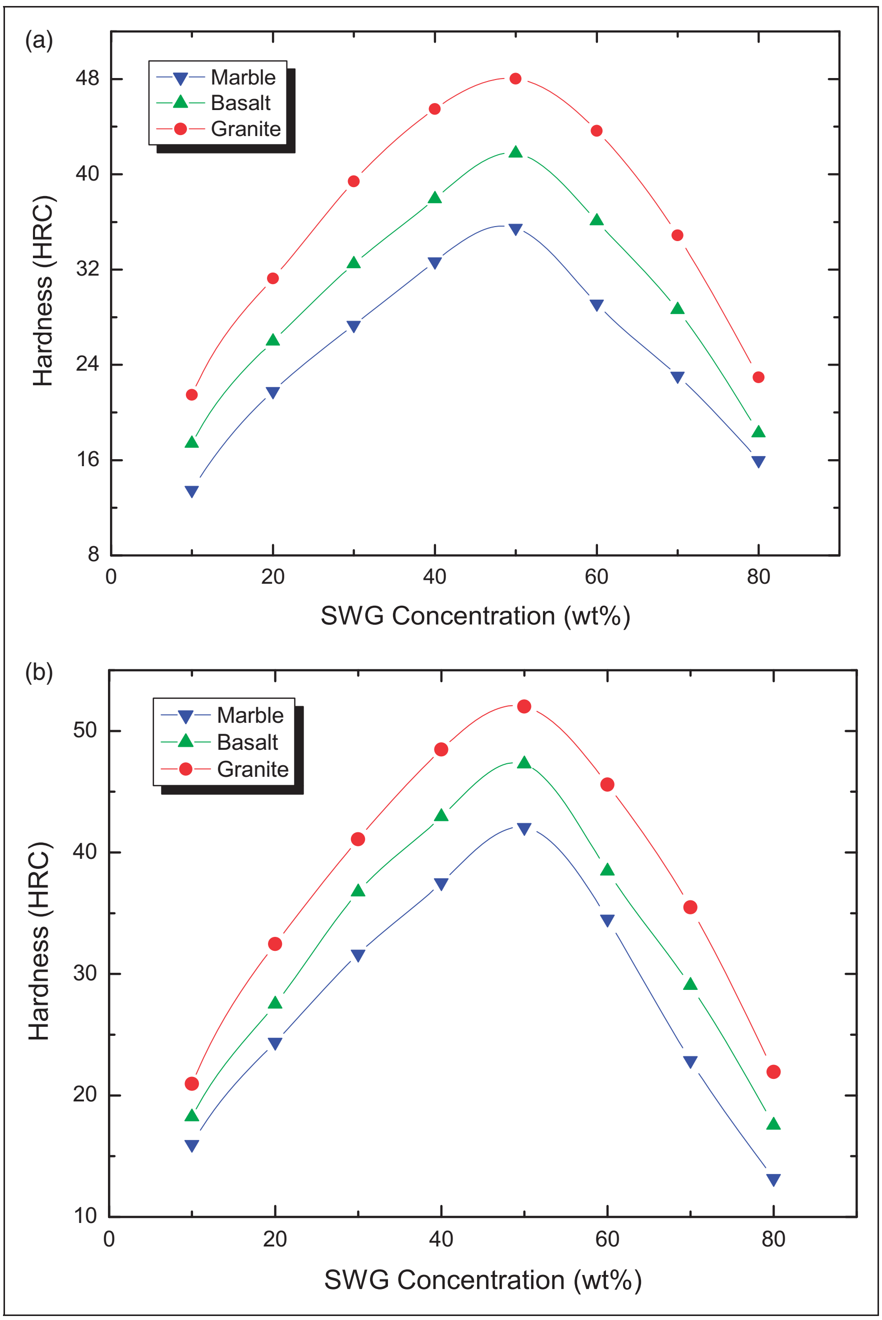

Figure 6. Effect of SWG concentration on the HRC of artificial stone samples based on (a) PMMA/SiO_2 and (b) PMMA/clay HNTs nanocomposites.

Table 2. The maximum values of HRC for artificial stone samples based on PMMA/SWG nanocomposites.

Stone	PMMA/nano SiO_2	PMMA/clay HNTs
Marble	35.49	42.06
Basalt	41.75	47.27
Granite	48.11	52.00

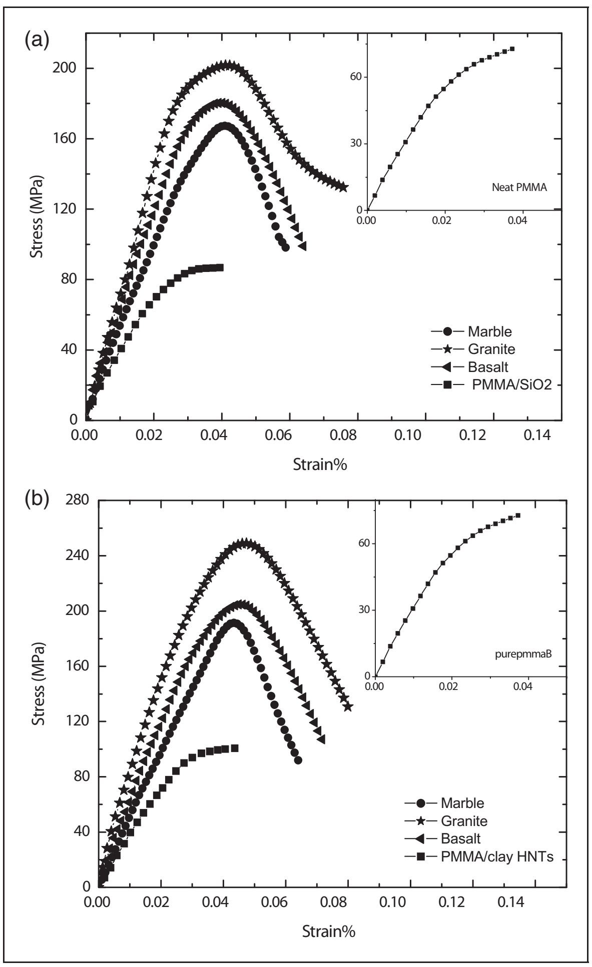

Figure 7. Flexural stress–strain curves of artificial stone samples based on (a) PMMA/SiO_2/SWG and (b) PMMA/clay HNTs/SWG nanocomposites compared to neat PMMA (inset).

Table 3. Effect of nanoparticle type on the flexural strength properties of artificial stone samples based on PMMA/SWG nanocomposites.

	E (10^3 MPa)		σ_m (MPa)		ε_m (%)	
Sample	Nano SiO_2	Clay HNTs	Nano SiO_2	Clay HNTs	Nano SiO_2	Clay HNTs
Marble	4.47	4.52	168.00	190.00	5.88	6.42
Basalt	5.20	5.37	179.32	205.00	6.40	7.10
Granite	6.56	6.80	201.46	251.00	7.60	8.10

Table 4. Flexural strength properties of PMMA before and after adding nanosilica and clay HNTs.

Sample	E (10^3 MPa)	σ_m (MPa)	ε_m (%)
PMMA	2.80	72.70	3.70
PMMA/SiO2	3.10	86.00	3.90
PMMA/clay HNTs	3.37	101.38	4.36

Table 5. Effect of nanoparticle type on the impact strength (kJ/m^2) of artificial stone samples based on PMMA/SWG nanocomposites.

Stone	PMMA/nano SiO_2	PMMA/clay HNTs
Marble	17	21
Basalt	20	23.6
Granite	23	26.8

Table 6. Effect of nanoparticle type on the abrasion percent of artificial stone samples based on PMMA/SWG nanocomposites.

Stone	PMMA/nano SiO_2	PMMA/clay HNTs
Marble	4.6	2.2
Basalt	3.2	1.9
Granite	2.0	1.0

PMMA/HNTs nanocomposite and granite stones in addition to its high impact strength compared to other stones.[25] The excellent compatibility and strong adhesion prevent the separation of SWG from the nanocomposite matrix and subsequently reduce the formation of cavities promoting the absorption of the impact energy.

The surface abrasion of PMMA/stone waste nanocomposites was estimated according to ASTM (D1044–08e1). Table 6 illustrates the percentage sample weight loss for all the prepared PMMA/SWG nanocomposites. It is noticed that the abrasion resistance is increased for the nanocomposies containing clay HNTs compared to those containing nanosilica. This advantage is a result of clay HNTs which are excellent non-corrosive materials that provide a large increase in the scratch resistance.[26] Granite waste stone showed the best candidate for scratch-resistant nanocomposites

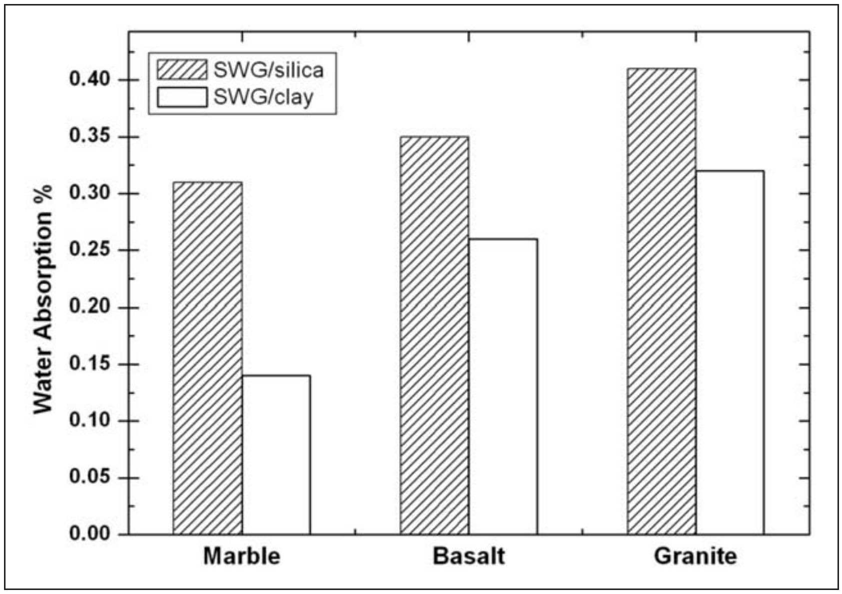

Figure 8. Effect of nanofiller types on the water absorption of artificial stone samples based on PMMA/SWG nanocomposites.

due to the fact that granite stones are rich in highly scratch-resistant crystalline phases.[27]

The water absorption was measured for artificial stone samples based on PMMA/SWG nanocomposites after 24 h of soaking at normal atmospheric conditions according to ASTM (D570–98 e1), and our results are plotted in Figure 8. It is observed that all the measured values are lower than those recorded for natural stones,[28] and this can be attributed to the fact that waste stones are protected from water diffusion after being completely saturated by PMMA nanocomposite solutions during the polymerization process. It is also noted that the water absorption for PMMA/stone nanocomposites based on clay HNTs is lower than those based on nanosilica. This can be attributed to the fact that HNTs have a larger longitudinal size compared to spherical nanosilica and consequently a longer penetration distance in the stone pores. In addition, adding both ATH and the cross-linking agents decreased the free volume of PMMA and prevents the presence of voids in the prepared matrix. Comparing the results of the investigated filling stones, it is clearly observed that the granite-filled nanocomposites have the maximum water absorption capacity compared to others. In the light of these results, it was found that MgO content as the chemical property and porosity as the physical property played a major role in the water-absorption capacity of granite stones.[29]

Conclusions

This study is focused on the preparation of innovative artificial stone sheets based on PMMA nanocomposites filled with SWG. The optimum concentration of SWG was determined by the study of HRC and found to be 50 wt%. Also, the flexural strength and impact toughness measurements showed the best properties for artificial granite sheet based on PMMA/SWG/clay HNTs nanocomposite. All the prepared sheets have the marmoreal appearance proved by luminous transmission measurements which showed enhanced diffused transmittance (45%) of artificial marble sheet based on PMMA/SWG/SiO_2 nanocomposite. The study revealed that PMMA/SiO_2 and PMMA/clay HNTs nanocomposites can be considered as potential host matrices for natural stone wastes to prepare artificial stone sheets, since the treatment of SWG with MMA/nanofiller solution enhances the rigidity and abrasion resistance of the solid surface product.

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