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Manufacturing Porcelain Covered BY (UPE/ Silica Fume) Gelcoat

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Abstract

Industrial porcelain and gelcoat samples were prepared. Two kinds of porcelain, soft and hard, have been prepared by adding the hardener with concentrations of 2.5% and 5% gm, respectively. unsaturated polyester that is reinforced with calcium carbonate ($CaCO_3$) with equal values. Also, a gelcoat was prepared using unsaturated polyester and silica fume (S.F.) that was added in different weight ratios (0.25, 0.5, 0.75, 1%). The mechanical and thermal properties of porcelain and gelcoat samples were studied; also, water uptake has been determined. The hardness values of soft porcelain and hard porcelain are 53 and 49, respectively, while the hardness value increased to a higher value (81.5) for selected gelcoat (UPE / 0.5% S.F). The impact strength values of soft and hard porcelain are 2.3332 kJ/m² and 2.666 kJ/m², respectively, and improved to a higher value (4.3 kJ/m²) by using gelcoat. Finally, a gelcoat improves the resistance to water diffusion for both types of porcelain after immersing in water for seven days.

Keywords: Porcelain, Gelcoat, Silica fume, Calcium carbonate.

1.Introduction

Unsaturated Polyester (UPE) was used in several applications due to its low cost, high strength, high glass transition temperature, good dimensional stability and ease of processing. Unsaturated polyester was brittle and had low impact strength because of its degree of crosslinking. To improve its mechanical properties, some additives were added in a fixed weight percentage to form new composites with good properties[1–3]. Calcium carbonate ($CaCO_3$) is one of the important additives that is used as a reinforcing filler in an unsaturated polyester matrix. This is due to its properties, such as its low cost and availability in nature or in markets in synthetic form. Also, silica fume is a good choice for some researchers to use as an additive to reinforce the thermosetting polymers such as epoxy and unsaturated polyester[4].The researchers in (2019) have been studying the mechanical and physical properties of (unsaturated polyester/glass fibre) composite reinforced with $CaCO_3$ with different weight percentages (2.5, 5, 7.5 and 10%) to improve the composite tensile properties[5].

In 2021, researchers have been studied the effect of the calcium carbonate ratio on the water absorption rate of (unsaturated polyester/calcium carbonate) composite, where water absorption increased with increasing the percentage of carbonate addition, the water absorption of (unsaturated polyester/5% calcium carbonate) increased to (31%) compared to neat polyester and tensile strength of (unsaturated polyester/1% calcium carbonate)[6].

In 2024, researchers have added (CaCO3) in different ratios (1-5 wt.%) to improve the ultimate compressive strength of unsaturated polyester. The percentage 3% of (CaCO3) is the best weight percentage, where the compressive strength of the (UPE) was about (74 MPa) improved to (~ 88 MPa) for unsaturated polyester reinforced by 3% (CaCO3)[7]. In this research, a synthetic porcelain that is used in floor and vase applications was prepared with high quality and low cost, and the improvement on some porcelain properties, a gelcoat of unsaturated polyester and silica fume was prepared as an external protective layer of porcelain.

2. Materials and Methods

2.1. Matrix

Unsaturated polyester resin named Siropol-8341, made by Saudi Industrial Resins Limited, has been used, with its accelerator (2% cobalt) and its hardener, methyl ethyl ketone peroxide (MEKP), with a concentration of 2.5% Wt (**Table 1**).

Table 1. The general properties of unsaturated polyester[3,8]

Appearance	Liquid
Color	Pale blue
Tensil strength (MPa)	41.4-89.7
Density (g/cm^3) a t 25°C	1.0852
Compressive strength (MPa)	>100
Electrical conductivity(mS/cm)	3.7

2.1.2.Fillers

2.1.2.1.Calcium carbonate

Calcium carbonate with a white color, as shown in **Figure 1** has a density of (2.71 gm/cm^3) with (Particle size of (50.23 nm) from the Indian company HIMEDIA

Table 2. properties of Calcium Carbonate [9].

Molecular formula	$CaCO_3$
molar mass	100.09 gm/mol
Appearance	white powder
Density	2.711gm/cm^3
melting point	1339°C

Figure 1. Calcium carbonate powder

2.1.2.2. Silica fume

Silica fume (SF) is an amorphous powder with a size of sub-microns and density (2.10-2.4) gm / cm3. From the German company Degussa.

Table 3. physical properties of silica fume [10].

Particle size	< 1µm
Bulk density	200-350 kg/m^3
Specific gravity	2.2
Specific surface	15.000 to 30.000 m^2/kg

Figure 2. Silica fume

2.2. Method

The porcelain was prepared by mixing 100 gm of unsaturated polyester with 100 gm of $CaCO_3$, and the hardener was added with two weight percentages (2.5 gm and 5gm) to get soft and hard porcelain, respectively. The porcelain mixtures were poured into silicone molds with (ASTM) dimensions and left to dry for 9 hours at room temperature before carrying out any mechanical or thermal tests.

To prepare an appropriate gel coat as a protective layer for porcelain, 100 gm of unsaturated polyester with different weight percentages (0.25, 0.5, 0.75, and 1%) of silica fume were mixed, and the hardener with a concentration of 2%, which means 2 gm of hardener, was added to the mixture before pouring it into molds and leaving it to dry for 1-2 hours at room temperature before carrying out any tests.

Table 4. The ratios of unsaturated polyester and silica fume in gelcoat

Unsaturated polyester	Silica fume
100g	0%
99.75g	0.25
99.5 g	0.5
99.25 g	0.75
99 g	1%

2.2.1. Hardness

The hardness values of porcelain (UPE/CaCO3) samples and gelcoats (UPE/SF) were determined using the Shore test model (D) (TH210) Italy. The test was carried out in the composite materials laboratory at the University of Technology.

2.2.2. Impact Strength

The Charpy impact test was carried out on porcelain and gelcoat samples according to international standard specifications (ISO-179) , as shown in **Figures 3 and 4**,respectively.

$$I.S = \frac{U_c}{A} \quad (1)$$ [11]

Where

U_C: is the fracture energy (Joules).

A: is the cross-sectional area of the specimen (m^2).

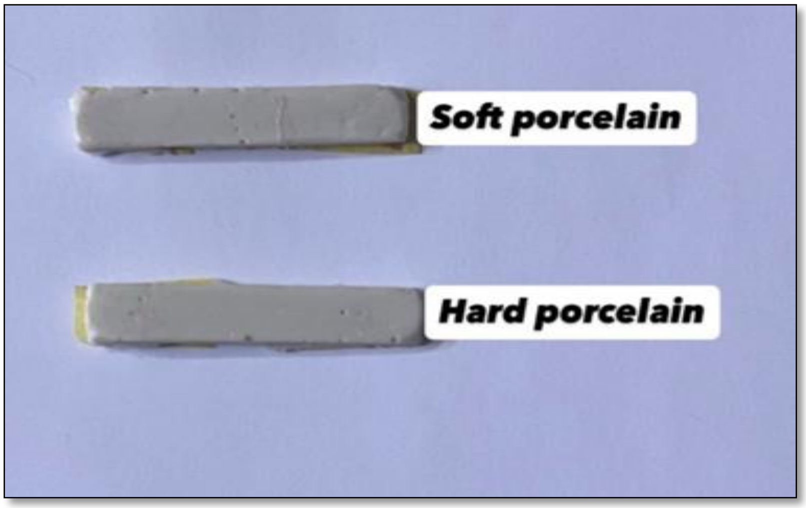

Figure 3. porcelain samples for impact test

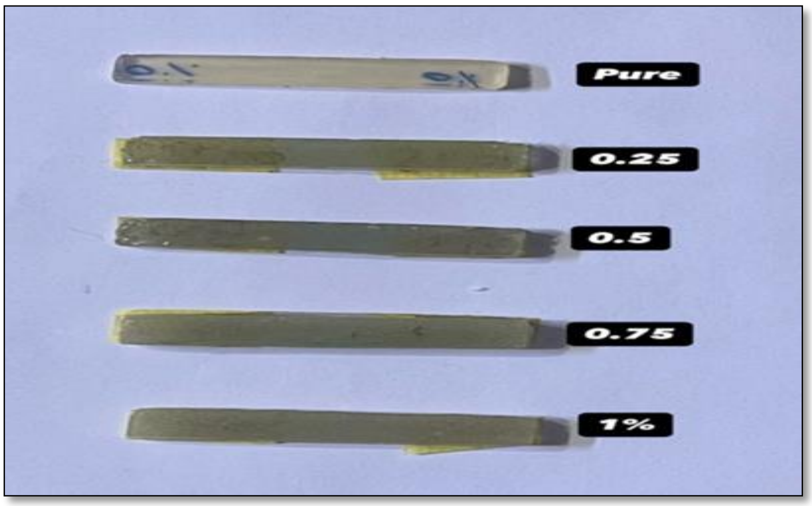

Figure 4. gelcoat samples for impact test

2.2.3. Thermal Conductivity

The thermal conductivity of porcelain and gelcoat samples was determined using a Lee disc device, supplied with a voltage of (6 V) and a current of (0.25 A).

The samples were made in a circular shape with a diameter of 40 mm, and a thickness of 3 mm, as shown in **Figures 5** and **6**. The test was carried out in the composite materials laboratory at the University of Technology.

Equations 2 and 3 were used to determine the thermal conductivity values of samples.

$$IV = \pi r^2 e (T_A+T_B)+2\pi re [d_A T_A + d_S \frac{1}{2}(T_A+T_B) + d_B T_B + d_C T_C] \quad \textbf{(2)}$$ [12]

$$K (\frac{T_B - T_A}{d_s}) = e [T_A+\frac{2}{r} (d_A+\frac{1}{4} d_S)T_A+\frac{1}{2r} d_s T_B \quad (3)$$ [12]

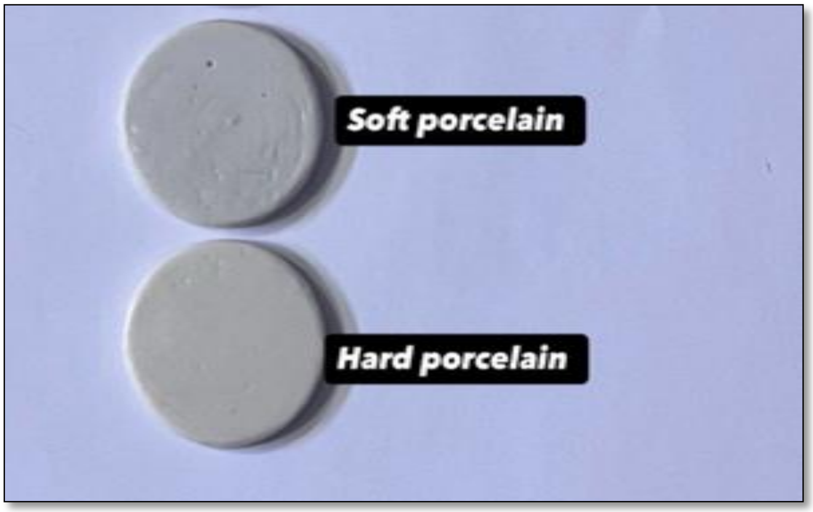

Figure 5. porcelain samples for thermal conductivity

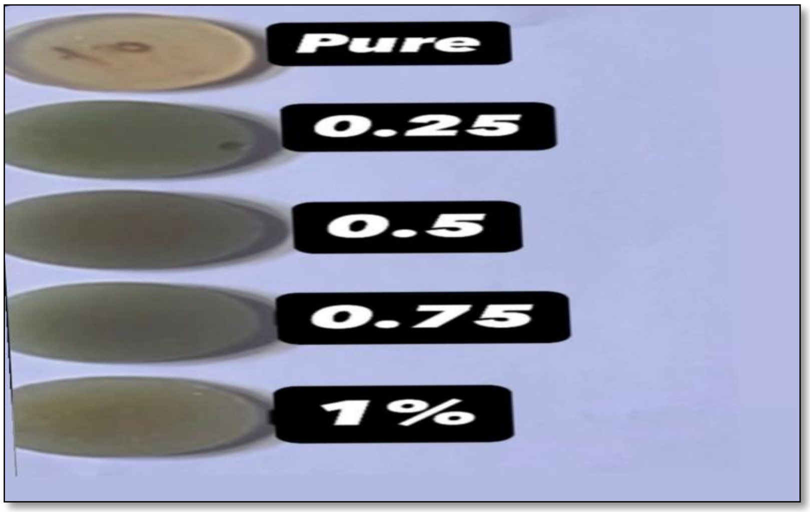

Figure 6. gelcoat samples for thermal conductivity

2.2.4.Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out on porcelain and gelcoat samples using a Shimadzu DTG-50 device with a heating rate of 10°C/min in a nitrogen atmosphere in a temperature range between 20 and 600 degrees Celsius. The test was carried out in Iran by Kak Laboratory.

2.2.5. Water absorption (E%)

The samples were weighed before and after being placed in distilled water for a week; the percentage of water absorbed (E%) was calculated using **Equation 4.**

E% = (weight of wet sample - weight of dry sample) / (weight of dry sample) × 100% (4)13.

3. Results

The hardness values of soft and hard porcelain and also the hardness value of pure unsaturated polyester, where the hardness value of soft porcelain is more than the hardness value of hard porcelain, as shown **Figure 7.**

Figure 8 shows the relationship between hardness values of gel coat with the weight percentage of silica fume, where the (UPE/ 0.5% S.F) is the best gelcoat according to its hardness value.

Figure 9 shows the impact strength values of pure unsaturated polyester with soft porcelain and hard porcelain, where the soft porcelain has a higher resistance to impact compared with hard porcelain.

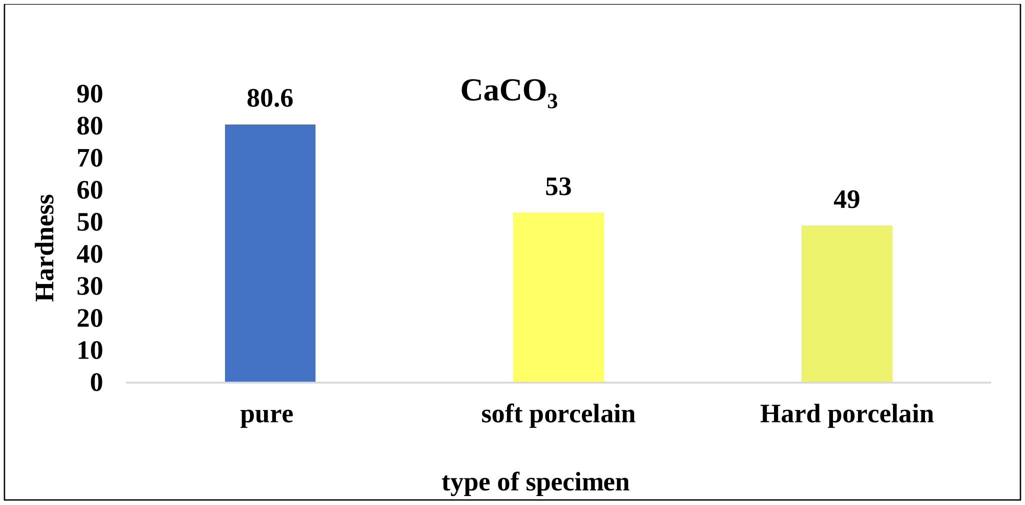

Figure7. Comparison of hardness values of soft porcelain and hard porcelain with pure unsaturated polyester

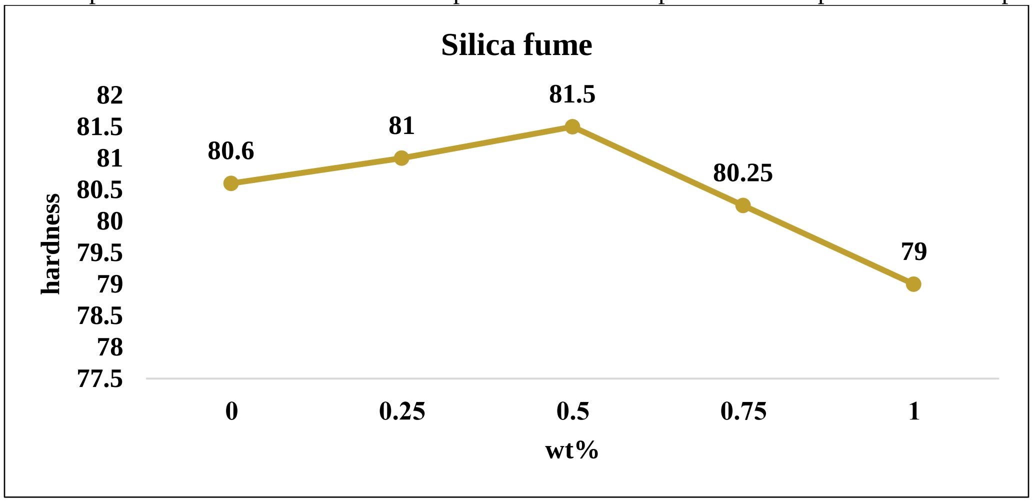

Figure 8. Variation in gel coat hardness values according to the percentage weight of silica fume

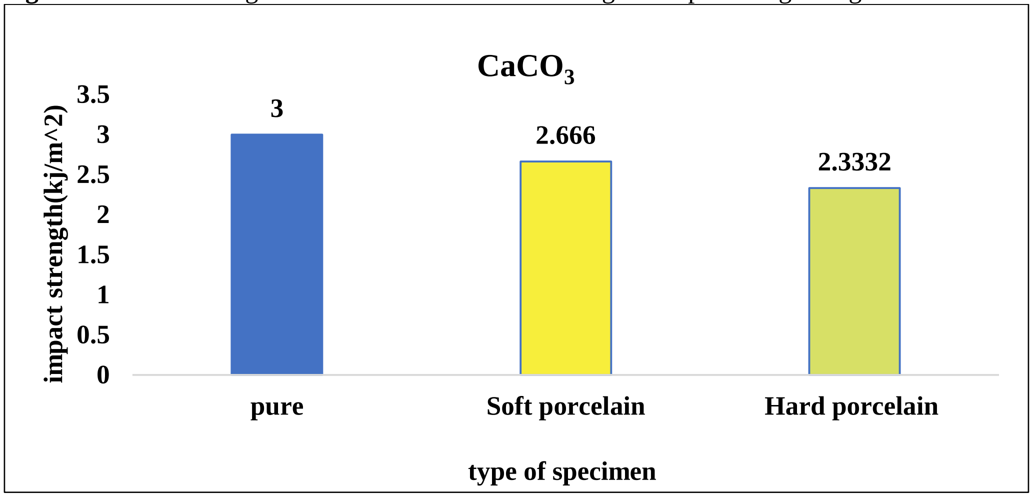

Figure 9. Comparison of impact strength values of pure unsaturated polyester with soft porcelain and hard Porcelain

Figure 10 shows the relationship between impact strength values of gelcoat with the weight percentage of silica fume, where the (UPE/ 0.5 % S.F) is the best gelcoat according to its impact strength value.

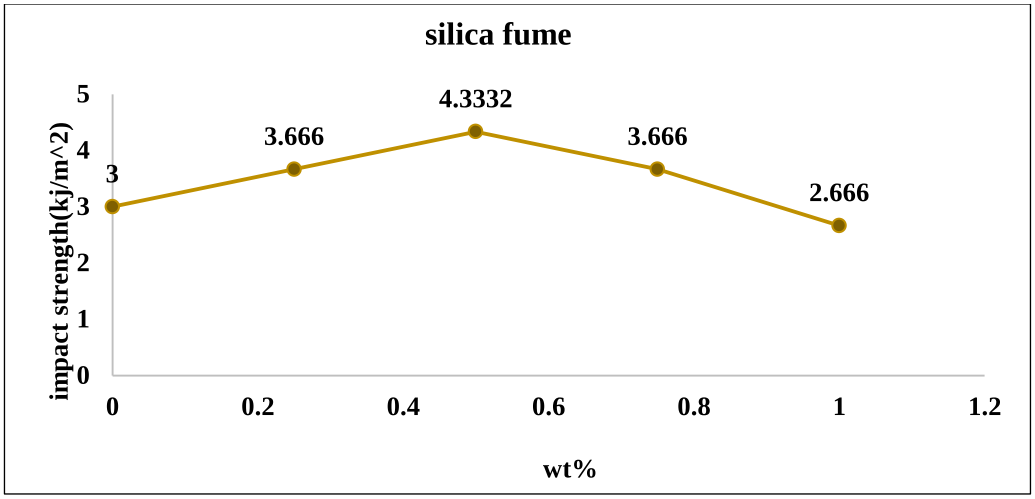

Figure 10. Variation in gelcoat impact strength values according to the percentage weight of silica fume

Figure 11 shows a comparison in thermal conductivity values of pure unsaturated polyester, soft porcelain and hard porcelain, where the soft porcelain has a lower thermal conductivity value.

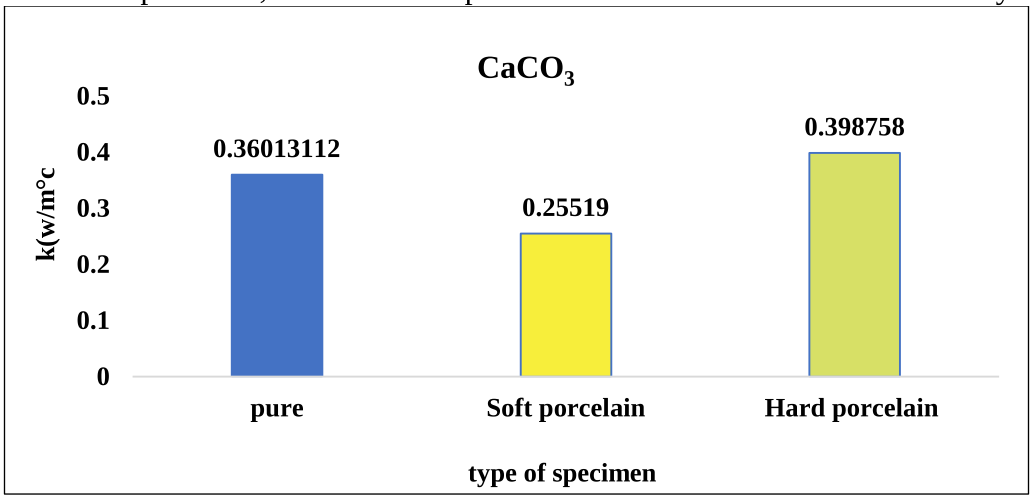

Figure 11. Comparison of the thermal conductivity values of pure unsaturated polyester with the thermal conductivity values of soft porcelain and hard porcelain

Figure 12 shows the relationship between thermal conductivity values of gelcoats with the weight percentage of silica fume, where 0.5% of silica fume is the best value.

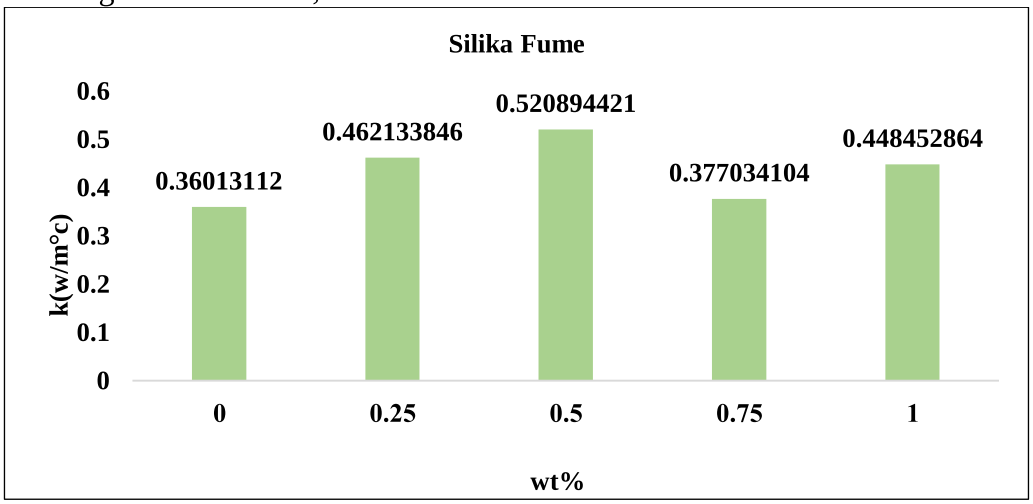

Figure 12. The thermal conductivity values of gelcoats vary depending on the weight percentage of silica fume.

Figure13 shows a comparison of the thermal stability of pure unsaturated polyester, gelcoat, soft porcelain, and hard porcelain, where the hard porcelain shows a higher thermal stability.

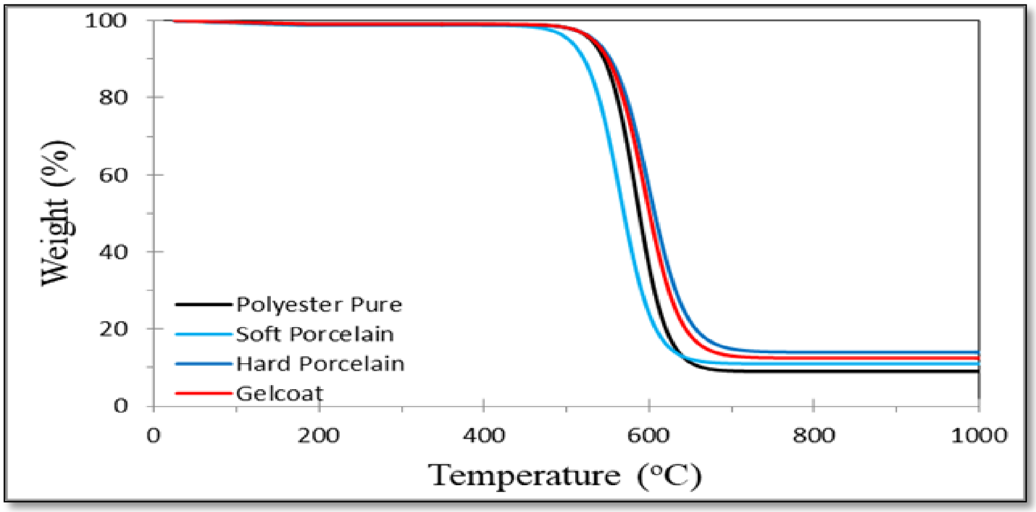

Figure 13. Comparison of the thermogravimetric analysis curve for pure unsaturated polyester and the optimal weight ratios for gelcoat, soft porcelain, and hard porcelain.

Figure 14 shows a comparison in water absorption of gelcoat, soft porcelain and hard porcelain, where the soft porcelain showed a higher water absorption.

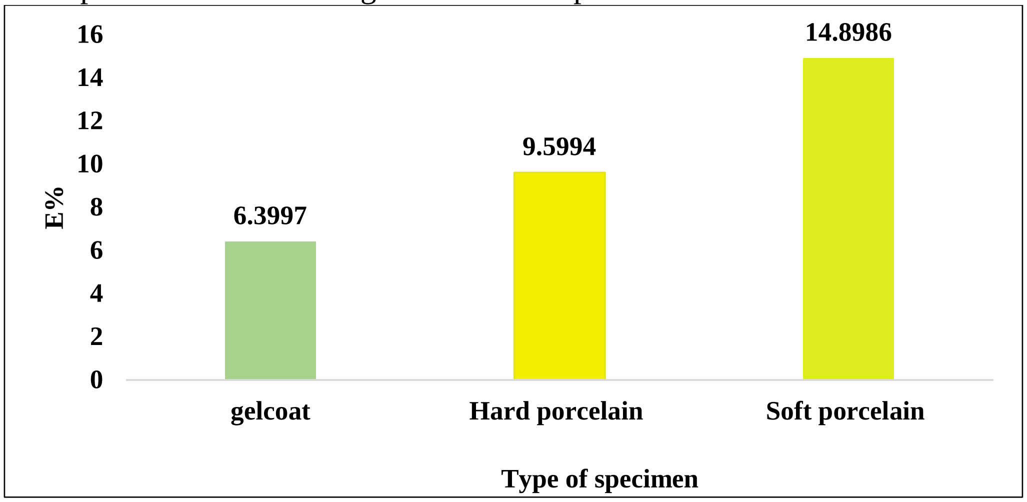

Figure 14. Comparison of water absorption of the best weight ratios of silica fume (gelcoat) with its values for soft porcelain and hard porcelain

4. Discussion

The resistance of porcelain and gelcoat samples to penetration is the hardness [8,14–17]. The hardness values of porcelain are lower than those of pure polyester, as shown in **Figure 7**. Also, the soft porcelain is harder than hard porcelain; this is because an increase in plasticity causes hardness in composite [18,19].

To increase the hardness values of soft and hard porcelain, a gelcoat of unsaturated polyester reinforced by silica fume have been prepared and select the best weight percentage of silica fume in this gelcoat to coated the porcelain. **Figure 8** shows that the silica fume with ratio (0.5 wt %) is the best weight ratio that increasing the hardness value of unsaturated polyester, this because ,firstly the silica fume has high hardness compared with those for (UPE), secondly the silica fume in ratio (0.5%) play as bridges between the chemical chains of unsaturated polyester , these two factors lead to success this gelcoat (UPE/ 0.5% Silica fume) as a good product layer for porcelain products, the hardness values of gelcoat that has a high hardness value (81.5) compared with the hardness values (53 and 49) of soft and hard porcelain, respectively. These results agreed with [20,21].

A Charpy impact test was performed on soft and rigid porcelain composites. **Figure 9** shows that soft porcelain have a higher value compared with that of hard porcelain, this may be due to elastic structure of soft porcelain, where the hardener that added was only (2.5%), which leads to a weak bonds between the matrix chains , so the structure of soft porcelain can absorb more impact energy before fracture, the impact strength value for soft porcelain decreases by 0.11% compared to pure polyester only, while for hard porcelain by 0.22% compared to pure polyester. This is due to calcium carbonate being a brittle material [22].

To get more improvement in the impact strength values of soft and rigid porcelain, the best (UPE/ S.F) gelcoat was used as a coat layer on the porcelain.

Figure 10 shows the impact strength values of gelcoats with different weight percentages of silica fume, where the (UPE/0.5% S.F.) gelcoat shows a higher impact strength value. This is because this gelcoat has a higher hardness, which mostly leads to a higher impact strength [23].The impact strength of gelcoat increases to twice that of soft and hard porcelain.

Figure 11 shows that soft porcelain was a very effective thermal insulation because it possesses a lower thermal conductivity value (0.255 Watt / m.c). This is because of its amorphous structure, which has weak bonds and more elasticity compared with unsaturated polyester with a brittle nature and also with hard porcelain with strong bonds and a more crystalline structure.

To increase the thermal conductivity values of hard porcelain, a good gelcoat is also used as an external layer for this porcelain. **Figure 12** shows that gelcoat (UPE/0.5% S.F.) has a higher thermal conductivity value (0.52 watt/m.c.). The figure shows that thermal stability decreases with a decrease in the hardener weight percentage in (UPE/$CaCO_3$) [16].

Figure 13 shows that polyester displays a sharp weight loss between 550 and 650°C and leaves a char residue of ~9 %) at 1000°C. By contrast, the composite containing silica fume exhibits a slight shift in the degradation profile towards higher stability, as indicated by the red curve. Moreover, the final residue increases to ~12%; this improvement is because of the inorganic nature of silica that remains thermally stable at high temperatures. This result shows the ability of even low filler loadings to restrict chain scission processes, enhance char formation, and improve high-temperature performance, making silica-reinforced polyester attractive for applications requiring enhanced thermal durability and dimensional stability under heat exposure[24–27].

Also, by comparing the thermal behavior of soft porcelain, hard porcelain, and gelcoat. All samples display a single-step major degradation process. The hard porcelain shows a significant increase in thermal stability compared with soft porcelain and gelcoat and higher residue than the pure matrix. This enhancement can be attributed to the dense ceramic structure of hard porcelain, which provides a more effective heat barrier[4].

This means that using gelcoat on soft porcelain will enhance its thermal stability, whereas hard porcelain already has higher thermal stability than gelcoat; therefore, hard porcelain does not require gelcoat as an external layer.

By immersing gelcoat, soft porcelain, and rigid porcelain in water for a week, as shown in **Figure 14**, it is observed that gelcoat exhibits a higher resistance to water absorption, while soft porcelain demonstrates a greater ability to absorb water. This increased absorption is due to the longer spaces between the chains of soft porcelain compared to those of hard porcelain. Consequently, soft porcelain requires more protection from gelcoat to prevent water absorption during one week of immersion. Also, water cannot penetrate the powder grains, so a lower water uptake is expected [28–30].

The addition of calcium carbonate to the unsaturated polyester leads to rising water absorption because the water absorption depends on the mixing base, and the density of calcium carbonate is higher than that of unsaturated polyester [13,31–34].

By adding calcium carbonate and hardener by the percentage (2.5%) to unsaturated polyester, water absorption will increase and the adhesion force between the unsaturated polyester matrix and calcium carbonate will decrease, and thus soft porcelain will contain more vacuums and be more porous [26]..

5. Conclusion

The hardener ratio in porcelain changes its properties; with a low weight percentage of hardener (2.5%), the porcelain (soft porcelain) becomes more electric and shows more resistance to external stress, such as hardness and impact forces, compared with higher rates of hardener (5%) that are used to prepare hard porcelain. So, to use the porcelain in flooring applications, the hard porcelain must be used, while for manufacturing the unbreakable antiques, the soft porcelain must be used. To provide better protection for the porcelain, a gelcoat made of unsaturated polyester reinforced with 0.5% silica fume is applied as an external layer to prevent or reduce water diffusion in the porcelain, while also increasing the thermal stability and conductivity of soft porcelain. That means the use of gelcoat for soft porcelain will increase its thermal stability, while hard porcelain has a higher thermal stability compared with gelcoat; therefore, hard porcelain does not need to use gelcoat as an external layer. By immersing gelcoat, soft porcelain, and hard porcelain in water for a week, as shown in **Figure 14**, the gelcoat demonstrates a higher resistance to water absorption, while soft porcelain exhibits a greater ability to absorb water due to the larger spaces between its chains compared to those in hard porcelain. This indicates that soft porcelain requires more protection from gelcoat to prevent water absorption during a week of immersion. Hard porcelain has higher thermal stability than gelcoat, so it doesn't require a gelcoat layer to increase its thermal stability. Conversely, adding a gelcoat layer to hard porcelain makes it more thermally conductive. However, adding a gelcoat layer to soft porcelain improves its thermal stability, and consequently, it doesn't require a gelcoat layer to increase its thermal insulation.

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Conflict of Interest

The authors declare that they have no conflicts of interest.

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We hereby confirm that all the figures and tables in the manuscript are ours.

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