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Characterization of Ceramic Waste Filled Unsaturated Polyester Resin

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Abstract*. In this study, the composites of ceramic waste filler polyester were produced with ceramic waste as the filler and unsaturated polyester resin as the matrix. Various weight of filler loads (particle size <180 μm) were used; 0, 28.5, 41 and 50 wt% in view to better understand the effect of filler content on the mechanical, thermal properties and water absorption of the composites. Additionally, Fourier transform infrared spectroscopy was used to characterize the samples, from the findings, it is noticed an increase in the level of porcelain powder decreased the flexural strength and Hardness and increased the density. The results of water absorption have shown the composites absorbs fewer water. Thermal degradation indicates that the composite is more resistant to temperature than unsaturated polyester matrix due to the effect of porcelain powder incorporated. Moreover, the results reveal an opportunity for using the ceramic waste as filler in unsaturated polyester resin formulation.*

Keywords*: unsaturated polyester resin, ceramic waste, Fourier transform infrared spectroscopy, mechanical properties, water absorption, thermal degradation*

1.Introduction

Recently, The scientific community aims to develop new kinds of materials for space structures that can resist the severe conditions of the spatial environment [1]. Composite products are made from a matrix reinforced using a wide variety of ceramic, metal or polymer fibres [2]. Unsaturated polyester resin is the most important matrix used in composite because it maintains an excellent balance enters the range of properties such as adhesion properties, electrical insulation properties, resistance to humidity, heat resistance, as well as mechanical properties. The performance of composites varies according to various parameters such as the properties of the polymers, kind of fillers and additives, the cure process and the dosage of the constituents. Nevertheless, the filler plays a major function in assessing the characteristics and performance of polymer composites [3].

The selection of a certain type of resin will depend on factors such as cost, desired properties and chemical/weather resistance.

The unsaturated polyesters (UP) are cross-linked in the presence of a monomer which also functions as the solvent, commonly styrene, in yielding the unsaturated polyester resins (UPR). The resulting viscous solution of UP and styrene can be transformed into a hardened product by means of a catalyst initiated free-radical copolymerization reaction between the styrene monomer and the unsaturated sites on the polyester backbone.

By-product and waste recycling is an urgent and rapidly emerging concern for the future of human kind [4], in this sense, different authors have proposed various solutions for the environment regarding the reuse of many types of waste [5-9]. Recently, a number of research studies have identified alternative ways of managing ceramic waste byreusing it in the production of alternative construction materials [10-12] or to develop new binding systems based on red clay bricks [13]. Utilization of distinct types of the waste in brick tile and the use of ceramic waste in different industries has been documented [4, 14-20].

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In addition, reusing ceramic waste has provided the construction industry with new advantages such as low cost, environmentally friendly and energy efficiency raw materials. The interest in using ceramic waste to replace other materials such as metals, wood, and virgin ceramics has increased markedly in the last decade. Indeed, several industries become very interested in applying these materials because of their unique characteristics [3, 21]. Nowdays, Increasing demand and the consequent rise in industrial production have resulted in a rapid reduction in the natural resources in Morocco. In addition, a high volume from production refuses or sub-products is also generates, the majority of which are not directly recyclable. Different requirements such as thermal, mechanical, acoustic, hydraulic properties as well as economic factors have to be satisfied when considering the durability of materials.

Reports on the utilization of porcelain powder prepared from ceramic waste taken from Settat region, as filler in unsaturated polyesters are not widely published. Hence, the goal of current research includes the development and the characterization of the Porcelain Powder and the Unsaturated Polyester Resin Composites.

2.Materials and methods

The resin had a density of1130 kg/m^3 and a viscosityof 500 cps at 25°C and 34% monomer content. Methyl ethyl ketone peroxide (MEKP) and octoate cobalt were used as an accelerant and catalyst, respectively. In terms of cost and ease of processing, the resin used in this study is suitable for the manufacture of sanitary products such as bathrooms, sinks, basins, etc.

Ceramic sanitary waste, such as basins, lavatory pans, bathrooms, and sinks were collected in public landfills in Settat city, Morocco. They were broken with a hammer and crusher to obtain a granular material with a particle size less than 4 mm in diameter. The powder was subsequently milled, dried in alumina media for 30 min (30% alumina balls, 30% ceramic waste, 40% air) to yield a porcelain powder (PP) with a mean particle size close to 180 μm.

The UPR was well mixed with appropriate quantities of porcelain powder (PP) for 10 min using a paste mixer. Then, the catalyst (2 wt%) and accelerator (0.5 wt%) were added into the mixture. The system was thoroughly mixed for an additional 10 min. Once the mixture was homogeneous, it was poured into a mold and placed under vacuum to prevent the formation of bubbles in the open air for 72h before demolding. The samples were prepared in different weight ratios of PP and resin where Sample1was pure polyester while Samples 2, 3, and 4 contained 28.5, 41.0, and 50% PP, respectively.

Key factors such as the dispersion and distribution f the filler as well as the adhesion and interface between the filler and the polymer matrix will affect the mechanical properties of polymer composites (22).

Density values (ρ) were calculated from:

$$\rho = \rho_0 \left(\frac{A}{A-B}\right) \qquad (1)$$

where ρ_0 is the fluid density (water), A is the sample weight in air, and B is the sample weight in liquid.

Hardness is dependent on ductility, elastic stiffness, plasticity, strain, strength, toughness, and viscosity. The capability of the composite material to resist abrasion or indentation is also known as hardness and a Rockwell hardness tester was used to measure the hardness of the composite. For Rockwell hardness testing, samples were prepared according to ASTM D785 [23]. The size of the indentation is the measure of the hardness of the sample. The standard test specimen shall have a minimum thickness of 6 mm. At least five hardness tests shall be made on isotropic materials. Prior to the hardness testing, the test object was polished to ensure a smooth surface. Rockwell hardness was measured using a hardness test machine. Each test object variation was performed with ten repetitions and five averaged to obtain the final value.

Flexural strength is the ability of the material to resist bending under applied load, however, for testing, samples were cut as per ASTM D-790-10 standard and tested for flexural strength by a universal testing machine.

Fourier transform infrared (FTIR) spectra in KBr pellets were collected on a Perkin Elmer (FTIR-2000) spectrophotometer, in the range of 4000-400 cm^{-1}. The (FTIR) was performed on significative sample powder.

Water uptake was measured by weighing the samples with an analytical balance followed by an immersion in water (which was kept at a constant temperature of 40°C). The samples were removed from the water, blotted, placed in a weighing bottle, and weighed using an electrical balance accurate to 0.1mg. After weighing, the samples were reemerged in the water bath.

Water absorption is expressed by:

$$\Delta m\ (t) = (m_t - m_0/m_0)*100 \qquad (2)$$

where Δm (t) is water absorption; m_t and m_o are the masses of the samples before and during aging, respectively.

The thermal behavior of the UPR and composites was examined using the TA instruments (labs TM Evo TGA-DTA 1600°C). The test samples, each weighing 25mg, were heated on a platinum pan from 25 to 600ºC with a heating rate of 10ºC/min. The thermal decomposition temperature of each sample was examined under argon with a 30 mL/min flow rate.

Then, temperature experiments were performed for different compositions at a temperature of 50, 100, 150, 190, 205, and 220°C for 24 h.

3. Results and discussions

The density of the samples increased continuously with increasing porcelain powder content (Figure 1). This is due to the higher density of PP compared to that of the matrix which resulted in the observed increase in composite density.

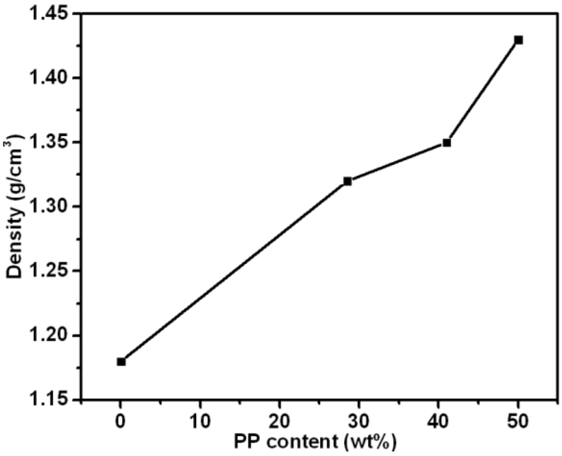

Figure 1. Density test result

It can be observed (Figure 2) that for an increase in level of PP result in a significant decrease in the hardness. The Rockwell hardness decreased to 76.6, 76.2, 75.8, and 74.4 with the addition of 0, 28.5, 41, and 50 wt% of the ceramic waste content, respectively (Figure 2). However, this decrease can be considered negligible.

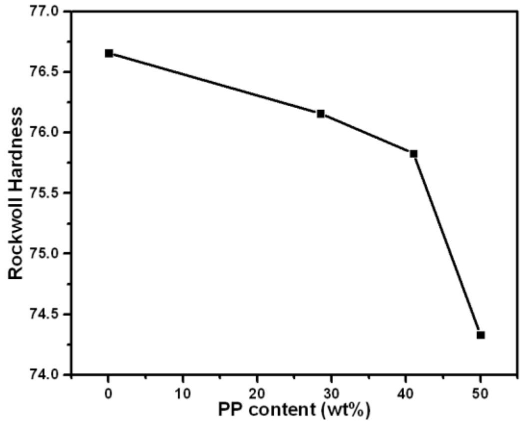

Figure 2.Hardness test result

Figure 3 depicts a decrease in Flexural strength when the quantity of porcelain powder increases; that is, when it has increased to 41wt%, the strength has slightly increased. The Flexural strength takes the values of 80, 49, 55 and 41 N/mm^2 when the incorporated quantity of PP is 0, 28.5, 41 and 50 wt%. This may be due to the insufficient adhesion between the porcelain powder and the resin. In addition, the unimprovement in flexural strength with the addition of PP can be due to its hygroscopic properties, which cause a high viscous mixture to formed if PP is mixed with the unsaturated polyester resin in production. This causes a reduction in the resin's wettability, and this in turn affects the mechanical properties resulting of composite.

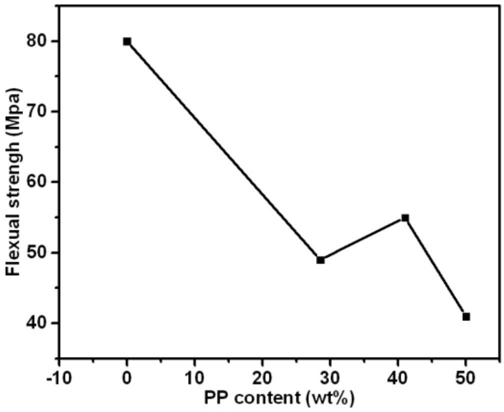

Figure 3. Flexural test result

In addition, it has been recognized that the difficulty in dispersing the filler is due to an increased in viscosity resulting from the formation of agglomerates acting as stress concentration and crack initiation sites [24].

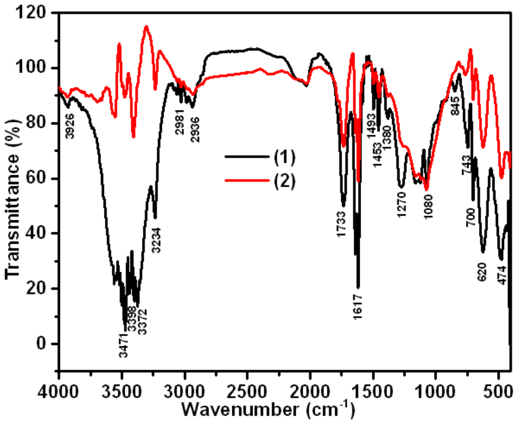

Figure 4. FTIR spectra of unsaturated polyester resin (1) and our sample with 50 wt% unsaturated polyester-modified resin (2)

The spectra FTIR show the observations IR data that are expected for the characteristic groups of our material samples (Figure 4). New material displayed all the bands which correspond to the resin networks without the presence of additional bands, which excludes any possible chemical interaction between the porcelain powder and the resin networks. The absorption peaks at 700 and 1733 cm^{-1} are representative of styrene (out-of-plane C-H bending in the benzene ring) and polyester (C=O stretching in the ester bond), respectively. An average absorption band at 1453 cm^{-1} has been attributed to C-H bending. The presence of the –C=O ester group corresponds to the peak at1733 cm^{-1}confirming the formation of polyester resin. The peaks at 2981 cm^{-1} represent the symmetric –CH stretching of resin. The band observed at 743 cm^{-1} indicates the presence of a-C-H band arising from1, 2 disubstitution in the benzene ring, the peak at 1080 cm^{-1} is indicative of the presence of bending of -C-H caused by the isomerization of maleic anhydride to fumarate which occurs in the polymerization process. In addition, the elimination of the anhydride peak at 1755 cm^{-1} in maleic anhydride and phthalic anhydride, plus the hydroxyl peak at 1375 cm^{-1} in propylene glycol, assures the formation of polyester.

Generally, we know that the moisture content increases with time which we could also observe in our experiments (Figure 5).

The Figure 5 indicates that water absorption has decreased while porcelain powder content in all the cases has increased. The percentage of water absorption for ten days for the specimen (1), (2), (3) and (4) of composites was 0.43%, 0.7%, 0.6%, and 0.4%.

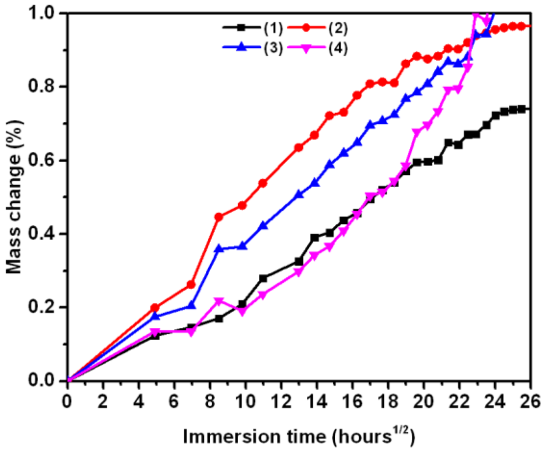

Figure 5. Weight gain in samples (1), (2), (3) and (4) at 40°C

A numerical analysis has indicated significant differences between the amount of water absorption (after 10, and 21 days of immersion in water) for each composite. The composite that contains 50% porcelain powder has the lowest water absorption or an immersion time below 504 h (Figure 5). After an immersion time of 504 h, it the materials that contain 28.5 wt% show lower water absorption compared to the other composites. For the mixture containing re-cycled ceramic and resin, the significant increase in water absorption suggests that the quality of the interface region in this mixture is more susceptible to water absorption. Thus, in order to be able to use recycled ceramics, it is required to use compatibilizers or coupling agents to improve the bonding between porcelain /resin powder and thereby enhance water resistance. We could thus show that increasing the PP rate has resulted in composites that were more resistant to water absorption and the new materials have only exhibited very small amounts of water uptake.

The filled samples had greater water intake when compared to that expected based on the resin content alone. This higher water absorption results in large part from the presence of porosity and filler particle aggregates in the microstructure of composites resulting from the mixing technique used to elaborate the composites. During the manual handling of the material. The air filled spaces that are introduced through the composite resin can result in inhibition zones being formed with uncured materials, leading in turn to a higher absorption of water [25]. In addition, the voids can be filled with water increasing the weight of the specimen. Nevertheless, the rate of water absorption depends also on the availability of water to composite resin product [26], in this case, water molecules first enters the open space produced by micro voids formed by cavities and then cracks in the matrix.

Composite systems are employed in a number of applications as a form of subject to a large range of variations in temperature; in this regard, it is extremely important to examine its thermal properties. In this context, it should be noted that composites such as those with a polymeric matrix and thermal characteristics are conditioned of both by the nature and properties of the polymer as well as by the reinforcement or additives or filler [27]. A thermogravimetric analysis (TGA) was carried out in an argon atmosphere to understand the effect of porcelain powder on the thermal stability of resin and composite materials.

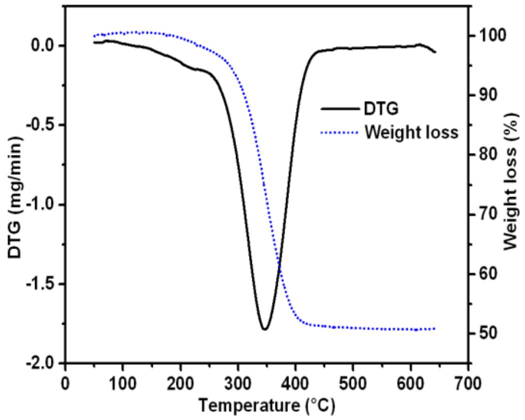

Figure 6. TGA/DTG curves for sample having 50wt% of PP when thermally degraded argon at 10°C/min

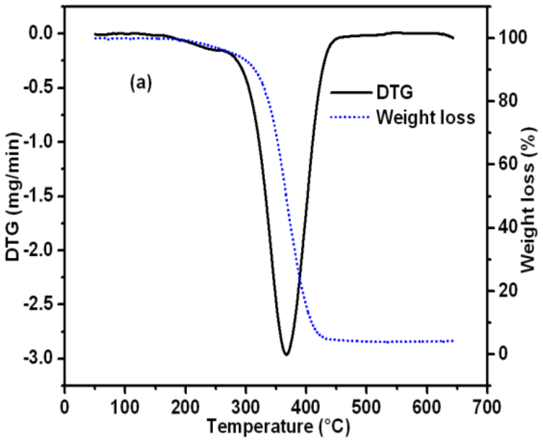

Figure 7. TGA/DTG curves for UPR when thermally degraded argon at 10°C/min

TGA thermograms show a thermal degradation pattern that is almost similar for every materials (Figures 6 and 7). In addition, TGA thermograms reveal an identical two-step thermal degradation process for two samples. For resin, the first stage begins at about 160°C with a peak decomposition rate of 0.168 mg.min^{-1} at 240°C. The maximal rate of decomposition in the second stage is 2.96 mg.min^{-1} at 367 °C, leaving a 4% residual mass at 440 °C. These results are consistent with previous findings [28]. For the composite, the first stage of degradation initiates just below 180°C, reaching a maximum rate of 0.142 mg.min^{-1} at 220°C. In the second degradation step, the maximum decomposition rate is 1.783 mgmin^{-1} reached at 347.9°C. The final mass at 440°C is 50%, which is considerably higher than for the resin. Evans et al. [29] used TG and DTA to demonstrate that different resins start to degrade at about 200°C with a significant weight losses occurring around 400°C.

These results show that the temperature at which degradation starts to occur for both resin and the composite lie above the typical maximum recommended service temperature of 60°C. Vankrevelen et al [30] noted that coal yield is a direct correlation with the potential for flammability retardation. Increased coal formation also has the potential to decrease the production of combustible gases, lower the exothermicity of the pyrolysis reaction, as well as inhibiting the thermal conductivity of the burning materials [31)].

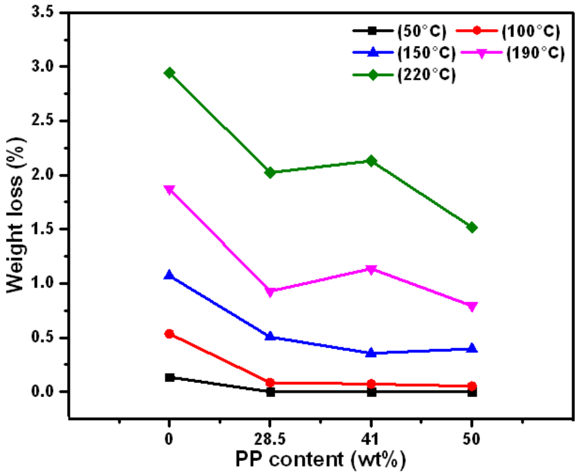

Figure 8. Weight loss of samples as a function of temperature

The weight loss for the processed materials increases as the temperature increases and decreases as the amount of porcelain powder incorporated in UPR increases (Figure 8).

This clearly indicates that while a lower filler load does not significantly improve thermal stability, a higher loading with porcelain powder retards thermal degradation of the composites and thus enhances temperature resistance. Composites prepared using PP exhibit a better fire resistance than UPR. The same improvement in fire resistance can also be achieved by increasing the amount of PP. This fully justifies the suitability of this new composite for domestic uses.

4.Conclusions

To conclude, this research mainly aims at investigating the feasibility of the use of ceramic waste for composite reinforcement, through which the experimental results of this investigation make us draw the following conclusions.

- Incorporation of porcelain powder in matrix causes a noticeable reduction in flexural strength and a small reduction in hardness.
- A FTIR analysis revealed the formation of PP reinforced polyester composites.
- The absorption values of the various materials remain almost very low for a long time at 40°C.
- From TGA results, it was observed that the composite was more resistant to temperature than the UPR due to the presence of porcelain powder.

In view of these results, porcelain powder produced by ceramic industry rejections maybe a good reinforcement in composite materials based on unsaturated polyester resin intended in domestic applications. All in all, as far as absorption and thermal resistance are concerned, the new materials should be highly suitable for domestic uses.

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