Destructive and Non-Destructive Tests of PET-Mortar Composites: Characterization by TG/dTG Analysis

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Reçu le:19/06/2014 *Accepté le : 10/04/2015*

Abstract—*This paper describes an innovative use of plastic bottle waste as cement-substitution within composite materials for preventing chemical attacks or repairing various reinforced concrete structures. So, the polymer-mortar composites have been produced by using polyethylene terephthalate waste (PET) at 0%, 2.5%, 5% and 7.5% ratios replace by CPJ-CEM II/A cement. The specimens were tested by destructive and non-destructive testing and for chemical resistance to acid solutions at different concentrations. From this study, it was found that the PET-modified mortars exposed to aggressive environments showed better resistance to chemical attack than unmodified one without substantially affecting the mechanical strength in tap water and UPV decreases as the proportion of PET waste in the mix increases. The addition of PET to the modified mortars, means reducing the penetration of aggressive agents. The formations which appear such as different calcium salts were determined by TG/dTG analysis. So, these composites are often used as low-cost materials for preventing chemical attacks or repairing various reinforced concrete structures exposed to aggressive environments where high resistance to acid is required and to both reduce sound intensity and dampen vibrations.*

Keywords: *Chemical Attacks, Mechanical Strength, PET, Polymer-Mortar Composites, TG/DTG, Ultrasonic pulse velocity.*

1. Introduction

Solid waste management is the prime concern globally due to ever increasing quantities of waste materials and industrial by-products. Various types of recyclable materials are currently used in civil

engineering applications. These materials include rubber waste particles [1,2], polyvinyl chloride (PVC) [3], PET [4-6], PET fibers [7], recycled polyurethane foam [8]. So, several works have been performed or are under way to evaluate the properties of cement-composites containing various types of plastic waste as aggregate, filler or fiber.

The use of plastic waste additives as particle replacement, as well as on site in concrete or mortar ready for use, is a practice unknown to the builders of our country. Therefore, we felt it important to study and evaluate the influence of these additions, substitutions such as cement, on the properties of hardened mortar or composite. Certain key proportions are also studied, in contrast with what has been undertaken in previous work [1,9,10] in order to determine feasibility limits. A PET waste polymer is used which is available considerable quantities in Algeria and must necessarily add value. For this we crafted four types of composite containing PET (0%, 2.5%, 5% and 7.5%), on which we measured the properties of PET-mortar composites by destructive and non-destructive testing and for chemical resistance to acid solutions at different concentrations. The formations which appear such as different calcium salts were determined by TG/DTG analysis.

2. Materials and Methods

The cement used was a blended Portland cement type CPJ-CEM II/A 32.5 delivered from Zahana factory located in the western Algeria, the 28-day compressive strength of cement was 32.5 MPa. The absolute density of the cement used was 3.15 g/cm^3 and specific surface area measured with Blaine method was 3532 cm^2/g. Initial and final setting times of the cement were 170 and 245 min, respectively, according to the manufactories. The chemical composition (Table 1) was obtained by using an X-ray fluorescence spectrometer analysis type OXFORD MDX^{1000}.

Tableau 1: Chemical composition properties of cement

Components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	L.O.I	CaO free
Mass (%)	21.93	6.81	4.26	63.87	0.21	1.31	1.83	0.13

The waste PET bottles used as particles were supplied from TRAMAPLAST PET Bottles Plant, in Tlemcen, Algeria. It is a semi-crystalline polymer, with a melting point of about 260°C. Its density (specific gravity) is around 1.3 - 1.4 g/cm^3. The PET powder is obtained by finely crushing the drink bottles (waste plastics). After preliminary tests, polymer particles of size lower than 1 mm were used in this study. Furthermore, the crushed sand obtained from Kristel quarry in Oran, West Algeria was used.

2.1 Composite Mixing Conditions

The mortar manufactured without PET particles was first optimized on the basis of mechanical criteria and then constitutes the reference composite. The composites containing PET waste were produced in accordance with our previous results [5]. A massic ratio of 3 between sand (S) and the cement (C) has been respected. Various massic percentages of cement (2.5%, 5.0% and 7.5%) were substituted by the same weight of granulated plastic waste. The water to binder ratio was kept constant at 0.5.

2.2 Destructive and Non-Destructive Tests

The relative acid attack was determined in accordance with ASTM C267-97 [11]. The mortar specimens were cured in water saturated with lime at 20 ± 2°C for 28 days before being subjected to acid attack. Three specimens of each mortar and composite mixes (50×50×50 mm^3) were immersed in five types of chemical solutions: 5% nitric acid (HNO_3); 5% sulfuric acid (H_2SO_4); The effects of the rain simulation have been investigated both in one water solution of sulfuric and nitric acid (molar ratio 3.4:1) has been used as acid rain; 5% phosphoric acid (H_3PO_4) and 3% fluoric acid (HF).

After immersion in acid solutions for the required period of time (ASTM C267-97 [11]) and before the test; the attacked composites were cleaned with deionised water and then the specimens were capped and tested for residual compressive strength based on the original cross-sectional area. The compressive strength loss (CSL) is calculated as follows:

$$CSL(\%) = \frac{f_{cr} - f_{cs}}{f_{cr}} \times 100 \qquad (1)$$

Where fcr is the reference compressive strength of specimen before immersion in the acid solution in MPa and fcs is the average compressive strength of the specimens after immersion in acid solutions for the required period of time.

Compressive strength test and ultrasonic pulse velocity test were conducted on 50 mm cube in accordance with ASTM C109-11 [12] and ASTM C597-09 [13], respectively. Tests were performed up to 180 days for ultrasonic pulse velocity “UPV” and to 7, 28 and 90 days for compressive strength in tap water.

After compression testing, thermogravimetry analyses TG/dTG were conducted on selected surface fractures to investigate damage mechanisms.

3 Results and Discussion

3.1 The relative acid attack

Mass loss is a simple traditional test in the context of acid attack. However, mass change results may depend on sample size and cement type, and are also influenced by the way the decomposed cement paste and other reaction products on samples are treated during testing. Therefore, along with mass loss test, compressive strength is considered to be a more reliable measure to judge the performance of mortar/concrete subjected to acid attack. Siad et al. [14] reported that there is some divergence between the mass loss and the compressive strength loss.

Hence, figure 1 presents the results of compressive strength loss CSL% of the mixes at 90 days in various acid solutions. The results indicate that the resistance of acidic attack of the composites was increased with an increase in PET content. At day-90, the CSL% of PET2.5, PET5 and PET7.5 were reduced by 8.5%, 5%, 22% for the water solution of sulphuric and nitric acid (molar-ratio of 3.4:1) when compared to that of PET0. One also noted a reduction by 3%, 2% and 16% for H_3PO_4 and by 17%, 8% and 21% for HF, respectively, when compared to PET0. In addition, there is a diminution around 4% for PET7.5 compared to an unmodified one in nitric and sulfuric solutions.

The increase in the resistance to acidic attack of the composites is attributed to the impervious PET granules blocking the passage of the aggressive solutions and the reduction of the sorptivity of PET-mortar composites. Furthermore, the decrease in porosity due to the incorporation of PET in modified mortars [15,16] contributes to reduce the absorption of acidic solution accompanied by a reduction of loss in weight. Additionally, different teams of researchers [5,17] reported that the incorporation of polymers increases chemical resistance in aggressive media.

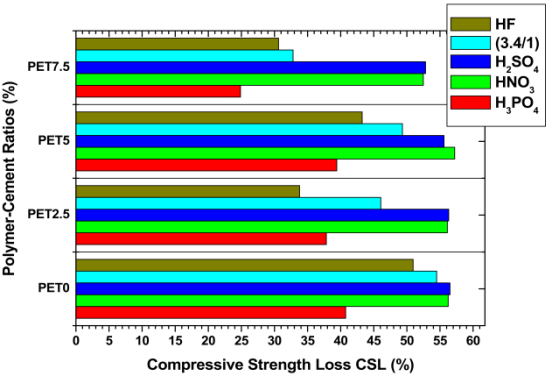


Figure 1: CSL (%) of specimens under acid solutions exposure.

These results are confirmed by the change of surface samples (PET0) before and after immersion in the aggressive solutions as depicted in Figures 2-4. A visual inspection of specimens revealed the deterioration of the samples, particularly for the mortars immersed in nitric, sulfuric, 3.4:1 and phosphoric acids. These mortars kept their cubic forms more or less, but their dimensions decreased considerably. Whereas, in the case of HF acid, there is a formation of white crystalline solid (single crystals are transparent) in the surface of specimens.

Figure 2: Deterioration of specimens after 7 weeks of immersion; (1) Tap water, (2) H_3PO_4, (3) HNO_3, (4) H_2SO_4, respectively. (From the left to right).

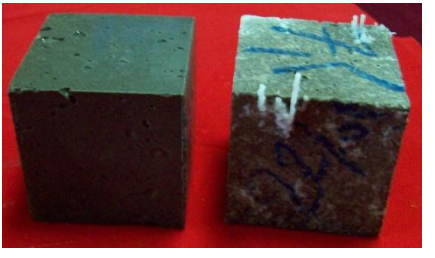


Figure 3: Deterioration of specimens after 7 weeks of immersion; (1) Tap water, (2) HF, respectively. (From the left to right).

Figure 4: Deterioration of specimens after 7 weeks of immersion in: (1) Tap water, (2) molar acid (3.4:1) solution.

3.2 Compressive strength and ultrasonic pulse velocity

Ultrasonic pulse velocity (UPV) test basically involve the measurement of electronic wave velocity through mortar or composite. So, The UPV through a material is a function of the elastic modulus and density of the material [18]. The UPV can therefore be used to assess the uniformity and quality of the material. UPV test was performed on composites at the age of 180 days. The results of the ultrasonic testing are shown in Table 2. UPV decreases as the proportion of PET waste in the mix increases for 180 days old specimens. This can be attributed to the formation of the products of the hydration of cement which fill any voids of the material that happen to exist. This is confirmed by other research teams [19]. It is also noted that the pulse velocity decreases by 2%, 13% and 18% for PET2.5, PET5 and PET7.5, respectively (Table 2).

However, PET favours the absorption of ultrasonic waves. Consequently, we may assume that constriction of UPV is also due to the presence of discontinuous air-voids. The ultrasonic wave bypasses these voids in order to propagate within the cement matrix. Thus, incorporation of PET particles into the cement matrix reveals the ability of composites to both reduce sound intensity and dampen vibrations, which serves to provide a reliable level of sound insulation.

Compressive strength results of composite mixtures with and without PET waste are shown in Table 2. It could be observed that composite mixtures made with PET exhibited lower compressive strength than control unmodified mortar. It was also observed that compressive strength of all composite mixtures increased with age. With the increase in age from 28 to 90 days, % increase in compressive strength of mixtures PET0, PET2.5, PET5 and PET7.5 were 14%, 21.5%, 9.6% and 21.4% respectively. Hence, Saikia and de Brito [20] reported that the factor that

may be responsible for low compressive strength of concrete/mortar containing plastic aggregate is: the hydrophobic nature of plastic waste, which can inhibit cement hydration reaction by restricting water movement.

Table 2: Effect of PET waste on compressive strength and UPV of PET-mortar composites

Mix design	Compressive strength (MPa)			V (m/s)
	7 days	28 days	90 days	180days
PET0	34.2 (±0.23)	41.61 (±0.35)	47.4 (±0.32)	3830
PET2.5	30.10 (±0.19)	38.66 (±0.43)	46.98 (±0.35)	3760
PET5	25.5 (±0.17)	36.69 (±0.39)	40.23 (±0.37)	3330
PET7.5	24.13 (±0.23)	32.49 (±0.40)	39.44 (±0.39)	3150

3.3 TG/DTG analyses

Figure 5(a) shows the TG/dTG curves of PET0 in the tap water. It can be seen that those curves consist of four zones:

~ 40°C - 123.3°C: dehydration of pore water,

~ 123.3°C - 420°C: dehydration of calcium silicate hydrates,

~ 450°C - 520°C: dehydroxylation of calcium hydroxide $Ca(OH)_2$,

~ 860°C: decarbonation of calcite $CaCO_3$.

Figure 5(b) shows the TG/dTG curves of PET0 in the HNO_3 acid. It can be seen that those curves consist of the following zones:

~ 100-145 °C: dehydration of pore water,

~ In PET0 composite there was no endothermic peak at ~450-500°C, which indicates that, with exposure all the $Ca(OH)_2$ that was formed reacted with the nitric acid solution (Eq.2).

$$2HNO_3+Ca(OH)_2 \rightarrow Ca(NO_3)_2.2H_2O \quad (2)$$

~ 860°C: there is a decrease of the peak intensity of decarbonation of calcite $CaCO_3$, which indicates that, with exposure some quantities of calcite that was formed reacted with the nitric acid solution (Eq.3).

$$2HNO_3 + CaCO_3 + H_2O \rightarrow Ca(NO_3)_2.2H_2O + CO_2 \quad (3)$$

Figures 5(c,d) present the TG/dTG trace for the surface part of the sample obtained from the PET0 composite stored in sulphuric acid and molar ratio (3.4:1) acid solutions; it displays the following endothermic peaks at ~150-160°C (High intensity) and 220 °C indicating gypsum and calcium monocarboaluminate hydrated, respectively. Also, TG/dTG analysis showed no endothermic peak at ~450-510°C, which indicates that, with exposure all the $Ca(OH)_2$ that was formed reacted with the sulphuric and molar acid solutions (Eq. 4). Furthermore, we also note that there isn't an endothermic peak at ~860°C who reveal the presence of calcite (Figure 5d), so this compound was decomposed by molar acid

attack. This is due to reactions of sulfuric and nitric acid (3.4:1) with the $CaCO_3$ (Eqs. 3 and 5). However, there is a decrease of this peak intensity in figure 5(c), which indicates that, with exposure some quantities of calcite that was formed reacted with the H_2SO_4 acid solution (Eq.5).

$H_2SO_4+Ca(OH)_2 \rightarrow CaSO_4.2H_2O$(gypsum) (4)

$H_2SO_4+CaCO_3+H_2O \rightarrow CaSO_4.2H_2O+CO_2$ (5)

Figure 5(e) presents the TG/dTG trace of PET0 after fluoric acid attacks; it displays four endothermic peaks, according to different reactions:

~ 100-145 °C: dehydration of pore water,

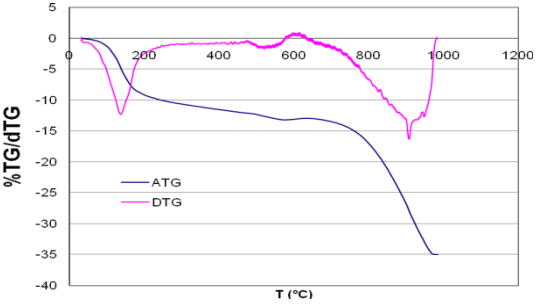
~ In PET0 composite there was no endothermic peak at ~450-500°C, which indicates that, with exposure all the $Ca(OH)_2$ that was formed reacted with the HF acid solution (Eq.6).

$2HF+ Ca(OH)_2 \rightarrow CaF_2+2H_2O$ (6)

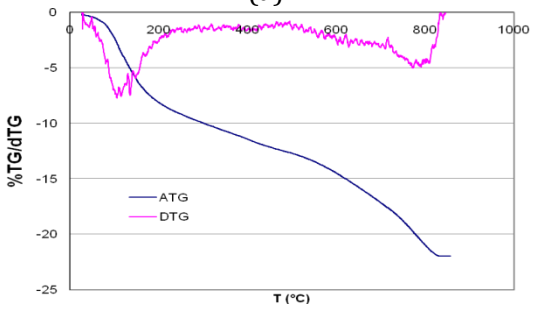
We also note that there isn't the peak at ~860°C who reveal the presence of calcite, so this compound was decomposed by HF acid attack. This is due to reactions of acid with calcium carbonate $CaCO_3$ (Eq. 7).

$CaCO_3+2HF \rightarrow CaF_2+CO_2+H_2O$ (7)

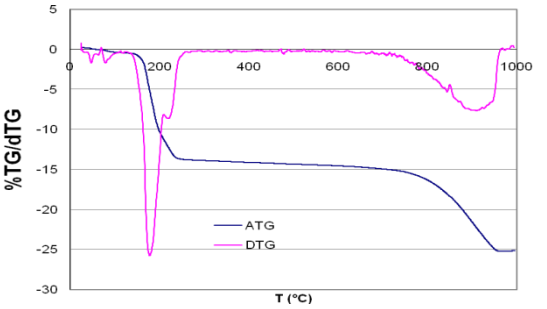
Hence, the TG/dTG analyses corroborate some of the results discussed above.



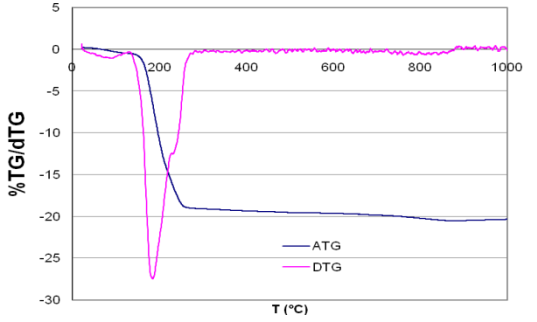
(a)



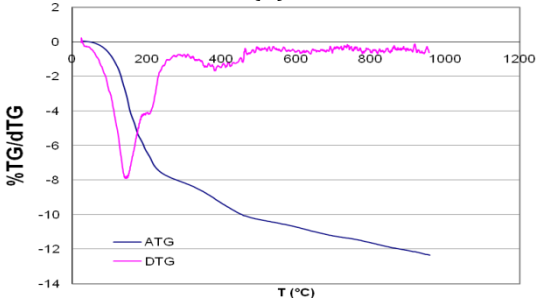
(b)



(c)



(d)



(e)

Figure 5: TG/dTG curves at 10 K/min of PET0 in: (a) H_2O, (b) HNO_3, (c) H_2SO_4 (d) (3.4:1), (e) HF acids exposure.

4 Conclusions

The results of this research prompt us to draw the following conclusions and considerations:

- The presence of PET lowers the detrimental effect of all types of acids on composite. Among composite mixes, PET7.5 mixes perform better than

other mixes. The course of action of acid attack is dependent on the type of acid present and for the solubility of the calcium salt formed.

- The UPV values of the PET-Mortar composites and compressive strength decrease with an increase in the percentage of the PET waste particles content. Thus, incorporation of PET particles into the cement matrix reveals the ability of composites to both reduce sound intensity and dampen vibrations, which serves to provide a reliable level of sound insulation.

- The formations which appear such as different calcium salts were determined by TG/DTG analyses.

The utilization of the PET waste as a binder instead of cement in the manufacture of such composites and as sustainable building materials in the construction industry help to cleaner environment and to both reduce sound intensity and dampen vibrations and for preventing chemical attacks or repairing various reinforced concrete structures.

Acknowledgments

The authors acknowledge the financial support from the Ministry of Higher Education and Scientific Research of Algeria, under the grants CNEPRU E01820120116. Also, the authors greatly appreciated the technical support from the LMDC Laboratory of INSA Toulouse (French).

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