Influence of High Temperatures on PET-Concrete Properties

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Summary: Lightweight aggregate is an important material in reducing the unit weight of concrete and it is essential in the construction of high-rise buildings; besides, the use of recycled PET bottles as lightweight aggregate in concrete is an effective contribution for environmental preservation. So, the objective of the present work is to study the flexural strength of PET-concrete and PET thermal degradation in the concrete, when the blends with 10 and 20 vol% of PET are exposed to different temperatures (200, 400, 600 °C). The flexural strength of PET-concrete exposed to a heat source is strongly dependent on the temperature, the water/cement ratio, as well as on the content and particle size of PET. Furthermore, the activation energy for PET degradation is affected by temperature, location of PET particles on the slabs and the water/cement ratio. A higher content of water gives rise to hydrolytic degradation on PET and a higher vapor pressure that increases the formation of cracks on the concrete. The values of activation energy are higher on the center of the slabs than on the surface, due to the poor heat conduction of concrete.

Keywords: activation energy; flexural strength; recycled PET; thermal degradation; water/cement ratio

Introduction

Generally, lightweight aggregate is made up of ground stones. However, this lightweight aggregate faces several problems: a) the high cost of the aggregate due to the high incineration temperature needed for grounding, b) the poor quality of concrete due to the shrinkage and resistance to freezing and thawing because of high absorption of the lightweight aggregate.[1] Therefore, the improvement of the quality of lightweight aggregate concrete has attracted much attention from researchers.[2–4]

Several million tones of Polyethylene Terephthalate (PET) post-consumer plastic waste reach the environment and only 7% is recycled to produce low-grade plastic products.[5–6] PET can be obtained from the recycling of bottles, which take more than 100 years to completely degrade. Thus, the use of PET-reinforced concrete materials is an effective contribution for environment preservation.[7]

In addition, fire continues to be one of the main threats to modern buildings. As concrete is a non-combustible material, the effects of fire on the properties of concrete are those caused by the exposure to high temperatures. Fire resistance of concrete is very heterogeneous because concrete is not only a composite material with components having different thermal characteristics, but it also has properties that depend on moisture and porosity, and it becomes even more complex when a lightweight aggregate such as recycled PET is added.

In this work, an experimental study was conducted on the flexural strength of the PET-concrete blends and on the thermal degradation of PET in concrete, when the blends with 10 and 20 vol% of PET were

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exposed to temperatures of 200, 400, and 600 °C. The initial decomposition temperature (Tid) of PET lies around 400 °C; therefore, it is convenient to study the behavior of the composite material within a range near the Tid, so as to determine the effect of its decomposition on the tensile properties for future applications.

On the other hand, PET-concrete is more susceptible to high temperatures than normal cement concrete because the synthetic viscoelastic resin (PET) used in concrete is more sensitive than the inorganic cement binder used in producing normal cement-concrete. However, despite this loss in strength, PET-concrete remains a strong material compared to normal cement concrete.

Experimental Part

In this study, the materials used were Portland cement, fine aggregate (river sand), coarse aggregate (crushed stone) and lightweight aggregate (recycled PET). Physical properties of the aggregates are shown in Table 1. PET was obtained from recycled bottles supplied by Inmadeca C. A.

The average sizes of PET particles used were 0.26 and 1.14 cm (small and big, respectively), determined from measurements done to micrographs by means of an electronic magnifying glass (Figure 1 and 2). Average scrap size was determined through a software application available in the laboratory. Melting and initial degradation temperatures and MFI were determined by means of DSC, TGA and rheological experiments, and the values obtained were 248 °C, 412 °C and 70 g/10 min, respectively.

Table 1.
Physical characteristics of fine (sand) and coarse (crushed stone) aggregates.

Characteristics	Coarse aggregate	Fine aggregate
Specific weight (g/cm^3)	2.70	2.57
H_2O absorption (%)	1.15	1.83
Compact unit weight (Kg/m^3)	1547	1848

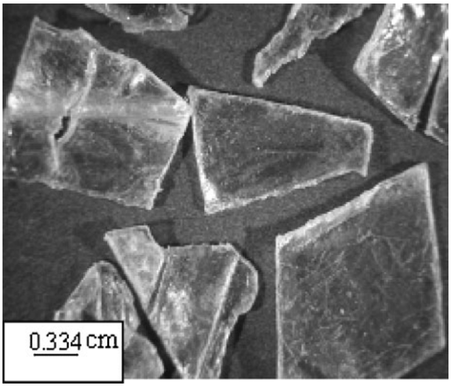

Figure 1.
Microphotograph of PET particles (large).

Fine aggregate (sand) was replaced with 10 and 20 vol/% of PET with scrap sizes of 0.26 and 1.14 cm and a 50/50 mix of both sizes. The mix design is presented in Table 2 for two different water/cement ratios (α), which were determined through a hydro balance; this implies that water and cement values presented in Table 2 are not the ones defining the water/cement ratio.

Concrete specimens (slabs) were prepared using metallic molds measuring 200 mm × 200 mm × 50 mm and compacted with a compaction steel bar. The specimens were covered with cling film to avoid water loss during the first 24 h; then, they were cured in a water tank at 25 ± 2 °C for 28 days after demolding.

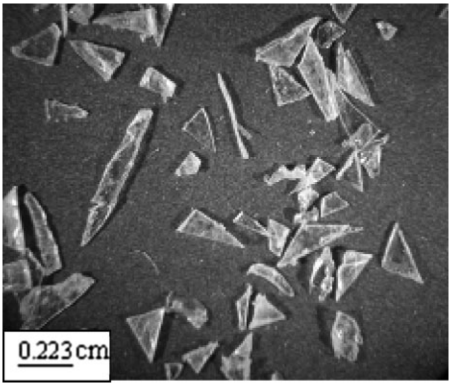

Figure 2.
Microphotograph of PET particles (small).

Table 2.
Mix design of the blends with different contents of PET and different water/cement ratios.

Components	Quantity (Kg)					
	$\alpha = 0.50$			$\alpha = 0.60$		
	Control	10% PET	20% PET	Control	10% PET	20% PET
Cement	24.10	24.10	24.10	19.10	19.10	19.10
Water	10.20	10.40	10.60	9.40	9.70	9.90
Sand	64.90	58.40	51.90	68.60	61.80	54.90
Stone	41.20	41.20	41.20	43.60	43.60	43.60
PET	--	3.40	6.90	--	3.60	7.30

A muffle furnace at a maximum temperature of 1200 °C was used. The cured slabs were placed in the cool furnace chamber. The temperature inside the furnace was increased up to 200, 400 and 600 °C, respectively; the slabs were kept at those temperatures during 2 h and then heating was stopped immediately. Three slabs per each blend were heated at each temperature. Specimens were cooled to room temperature and tested for flexural strength. In parallel, unheated specimens were tested. Additionally, a qualitative study by means of a visual inspection of the surface was performed on the slabs exposed to the different temperatures. Flexural tests were conducted as per COVENIN 343. In this test, the slab edges are placed on supports and a load is applied on the center line. The flexural strength values obtained show a deviation lower than 10%.

In order to determine activation energy (Ea), PET particles were extracted from the surface and from the center of the slabs, and a thermogravimetric analysis (TGA) was performed using a Mettler Toledo analyzer in nitrogen at heating rate of 10 °C/min, from 25 °C to 700 °C. Activation energy (Ea) was calculated from the data obtained, using the E2 function method.[8]

Results and Discussion

There are changes on the properties analyzed for the PET and for the concrete blends when they are exposed to different temperatures. Figure 3 and 4 show the flexural strength values for the different blends. It can be observed that while the substitution of the fine aggregate by the PET is greater, the strength of the slabs is lower, regardless of the temperature. However, even though the flexural strength decreased, the two parts of the slabs remained together (Figure 5).

Table 3 shows the activation energy values for PET corresponding to the blend with 10 vol% of PET of a 50/50 blend of both sizes (small and big), exposed to different temperatures. The other blend results are not shown since other PET particle size (only small and big) contents show values similar to those presented in Table 3.

It is worth noting that when the temperature at which slabs are exposed increases, the activation energy of the PET decreases. This effect is more pronounced for PET particles located on the surface of the slabs, since at the center, the particles do not reach the oven temperature, but a lower one. This change as a function of temperature was also observed by Li et al.[9] in high-strength concrete. Similar behaviors were detected by Hernández-Oliveira and Baluenga[10] in rubber-concrete blends. Concrete has poor heat conduction; therefore, concrete has a temperature distribution field inside. Consequently, temperature in the center of the concrete is much lower than that on the exposed surface.

The decomposition temperature of the unheated PET in the slabs ranges between 350 and 450 °C, obtained through a TGA essay. According to Gullon et al.,[11] within this temperature range, PET maximum degradation occurs, with a weight loss of

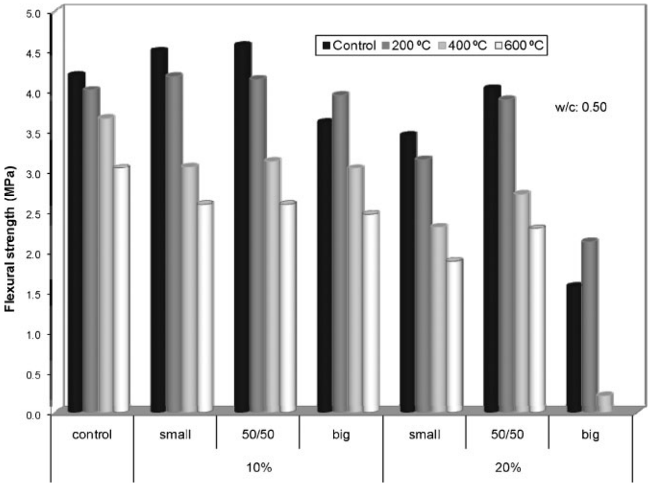

Figure 3.
Flexural strength of the PET-concrete blends with a water/cement ratio of 0.50 exposed to different temperatures.

80% due to random chain scission. So, at the exposure temperature of 200 °C, flexural strength values for the PET-concrete blends (Figure 3 and 4), specifically with PET contents of 10% for the different particles sizes, are very similar to those of the control blend. At 200 °C, concrete does not show significant variations in its structure, so, flexural strength loss is not substantial. In addition, no changes in the slab surface morphology were observed at that temperature.

At higher exposure temperatures (400 and 600 °C), PET decomposition occurs via random scission of the ester links involving a six-membered cyclic transition state to yield a vinyl ester and carboxylic acid-ended oligomers; these volatile oligomers undergo secondary decomposition reactions in the gas phase to give CO, CO_2, C1-C2 hydrocarbons, aliphatic aldehydes and aromatic hydrocarbons, acids, ketones and esters.[12,13] These volatile products are produced in greater extent at higher

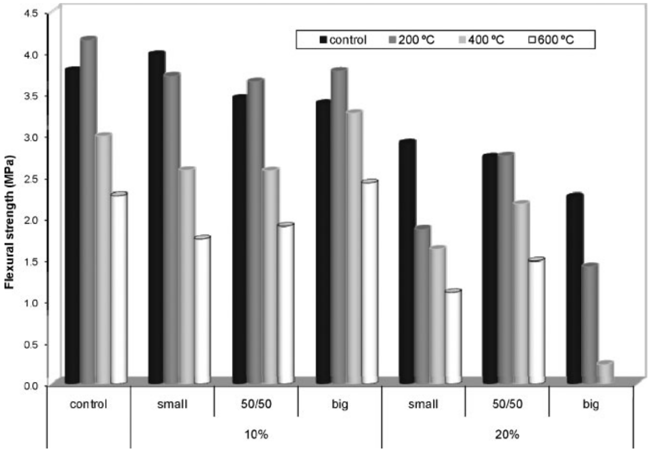

Figure 4.
Flexural strength of the PET-concrete blends with a water/cement ratio of 0.60 exposed to different temperatures.

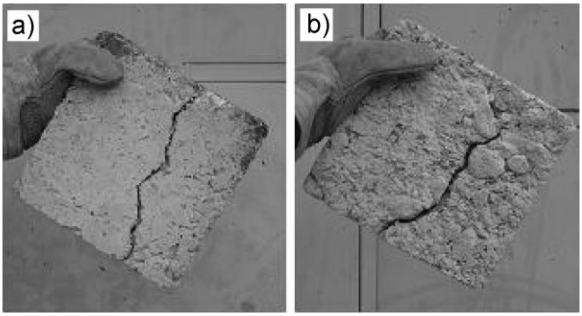

Figure 5.
PET-concrete blend slabs after flexural testing, a) 10 vol% PET; b) 20 vol% PET.

temperatures, giving rise to greater porosity (holes) in the concrete, hence reducing flexural strength.

The volatile oligomers produced during PET decomposition also react and give a crosslinked char through reactions of the vinyl ester groups with benzene rings.[14] These particles separate from the concrete paste, and as a result fissures and holes appear and flexural strength decreases.

With respect to concrete, the calcium hydroxide in the concrete starts to dehydrate and to transform into calcium oxide at exposure temperatures of 400 and 600 °C. The cracking can be attributed to the rehydration of dissociated calcium hydroxide, resulting in a volume increase.[15,16] Also, severe cracking of the heated concrete occurs during post-cooling; besides, the removal of the free water results in thermal stress, thus favoring the formation of cracks.

Figure 6 shows, as an example, the slab surface morphology of the blend with 10 vol% of PET with a bigger particle size, exposed to 200 °C. It can be seen that no significant variations are observed when compared to the unexposed blend. Qualitatively, this implies that at this temperature, few chemical reactions take place and the mechanical properties of PET-blend are not affected.

Figure 7–9 show the change on the slab surface morphology, responding to the blend with 10 vol.% of PET with different particle sizes, for both water/cement ratios (α: 0.50 and α: 0.60). Specifically, they exhibit a change of color from gray (characteristic color of concrete) to brown when exposed to temperatures equal or greater than 400 °C. This is due to the chemical reactions that take place between the materials that compose the concrete mix, as well as to the degradation and surface debonding of PET particles.

Nonetheless, for the blends exposed to 600 °C the surface PET is degraded, presenting a white color. This fact can be better observed in the slabs with a larger PET particle size (Figure 9).

Table 3.
Activation Energy (kJ/mol) of the blends with 10 vol% of PET with 50/50 average particle size.

Temperature (°C)	$\alpha = 0.50$		$\alpha = 0.60$	
	surface	center	surface	center
25	155	155	155	155
200	129	145	122	141
400	122	139	115	130
600	116	130	108	121

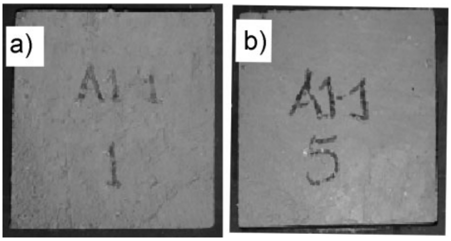

Figure 6.
Slab surface morphology with 10 vol% of PET with a bigger particle size and a water/cement ratio of 0.5, exposed to temperature. a) room temperature; b) 200 °C.

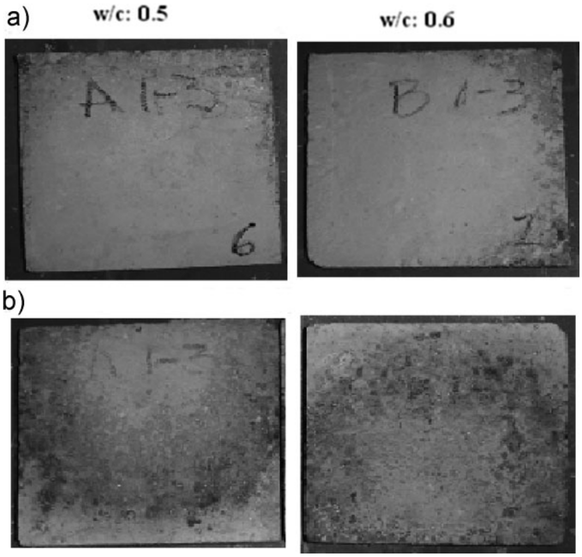

Figure 7.
Slab surface morphology with 10 vol% of PET with a smaller particle size and a water/cement ratio of 0.5 and 0.6, exposed to temperature. a) 400 °C; b) 600 °C.

When PET content increases up to 20 vol%, a more pronounced decrease occurs in the flexural strength, which is due to the increased formation of holes (stress concentration sites) as a consequence of the PET decomposition process.

Similarly, the slab surface morphology corresponding to the blends with 20 vol% of PET for both water/cement ratios changes, once the slabs are exposed to high temperatures (400 and 600 °C). The slabs also change color from grey to brown, with degradation and surface debonding of PET particles; this effect is more marked at 600 °C.

Furthermore, the authors do not report the flexural strength of the blend with 20 vol% of PET and a larger particle size at

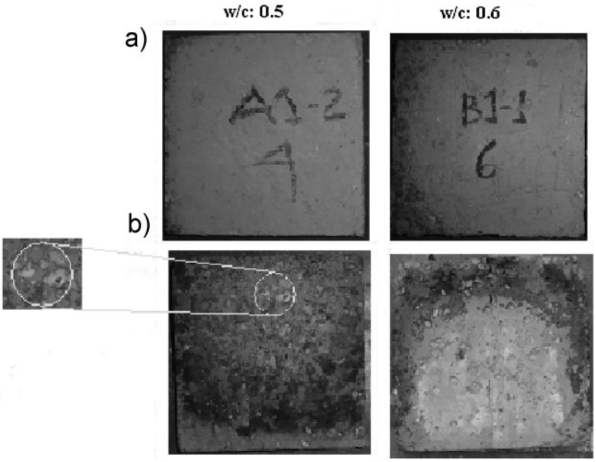

Figure 8.
Slab surface morphology with 10 vol% of PET with a 50/50 particle size and a water/cement ratio of 0.50 and 0.60, exposed to temperature. a) 400 °C; b) 600 °C.

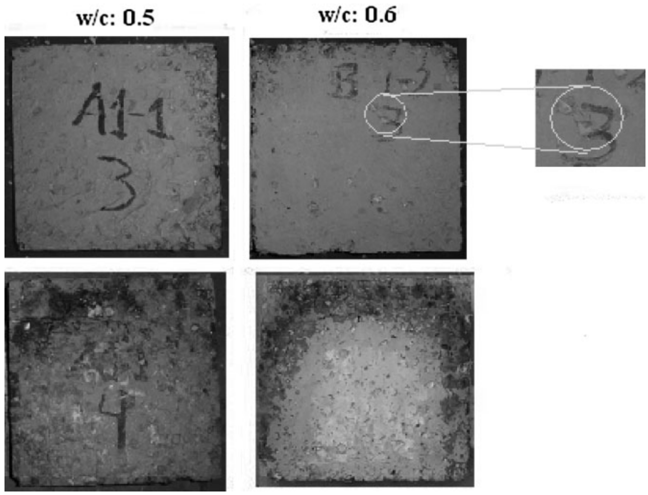

Figure 9.

Slab surface morphology with 10 vol.% of PET with a bigger particle size and a water/cement ratio of 0.50 and 0.60, exposed to temperature. a) 400 °C; b) 600 °C.

600 °C for both water/cement ratios, since the slabs fractured when they were removed from the oven, and so the test could not be conducted. Expansion occurs in some of the components of the cement, such as (SiO_2) that shows changes in its structure. According to Li et al.,[9] the shape of the crystals changes, thus giving rise to a volume expansion of the concrete of 0.85%. Similarly, the dehydration process of $Ca(OH)_2$, as well as the shrinkage caused by dehydration of the cement paste, result in a volume change of 0.5%.[18] This volume change and the degradation of the bigger content of PET particles result in less cohesion between concrete components and a greater number of holes that bring about the fracture of the slabs when they are removed from the oven.

When comparing the flexural strength values of all the blends obtained at different water/cement ratios, they show a similar behavior (Figures 3 and 4), and it is slightly lower for $\alpha = 0.60$. The activation energy values show a similar behavior, because a greater amount of water is present, which at high temperatures brings about PET hydrolytic degradation, thereby forming carboxyl and hydroxyl end-groups from the reaction of one water molecule with one PET unit. All these end groups tend to decrease PET thermal stability, thus accelerating PET decomposition; as a result, activation energy values decrease.[13,17] Besides, the water vapor is difficult to be discharged at high temperatures, so vapor pressure favors the formation of cracks in the concrete. Subsequently, concrete properties are impaired.[9]

Finally, it could be inferred that PET degradation process that brings about holes and gasses, as well as thermal stresses, results in the formation of many microcracks and macrocracks, thus diminishing the flexural strength at high exposure temperatures.

Conclusion

The flexural strength of PET-concrete blends, when exposed to a heat source, is strongly dependent on temperature, the water/cement ratio, and the content and size of PET particles. Activation energy, in turn, is influenced by temperature, the PET particle location in the slabs and the water/cement ratio.

The values of activation energy are higher in the center of the slabs than on the surface, due to the poor heat conduction of concrete. Besides, they decrease when exposure temperature increases, being the effect more marked for the blends prepared with a water/cement ratio of 0.60, since PET presents hydrolytic degradation in the presence of water.

At 200 °C, no significant changes are observed in the morphology and the flexural strength of the PET-concrete blends, even though the PET activation energy decreases when compared to the unexposed blends.

At higher exposure temperatures (400 °C and 600 °C) the PET degradation process gives rise to the formation of gas products, which provoke holes in the slabs, and to a volume expansion; as a consequence, internal stresses increase thereby diminishing flexural strength.

Concerning the influence of the water/cement ratio, results obtained show lower flexural strength values for a higher ratio (0.60), since higher water contents bring about thermal and hydrolytic degradation of PET and a higher vapor pressure on the concrete that enhances the formation of cracks.

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