

Waste Polyethylene terephthalate flakes modified by gamma rays and its use as aggregate in concrete



Gonzalo Martínez-Barrera^{a,*}, Liliana Ávila-Córdoba^b, Fernando Ureña-Núñez^c, Mar Alonso Martínez^d, Felipe Pedro Álvarez-Rabanal^d, Osman Gencil^e

^aLaboratorio de Investigación y Desarrollo de Materiales Avanzados (LIDMA), Facultad de Química, Universidad Autónoma del Estado de México, Km.12 de la carretera Toluca-Atlaquilco, San Cayetano 50200, Mexico

^bFacultad de Ingeniería, Universidad Autónoma del Estado de México, Av. Universidad S/N, Cerro de Coatepec, Ciudad Universitaria, Toluca, Mexico

^cInstituto Nacional de Investigaciones Nucleares, Carretera México-Toluca s/n, C.P. 52750 La Marquesa Ocoyoacac, Estado de Mexico

^dDepartment of Construction and Manufacturing Engineering, University of Oviedo, 33204 Gijón, Spain

^eCivil Engineering Department, Faculty of Engineering, Bartın University, 74100 Bartın, Turkey

HIGHLIGHTS

- Cement concrete specimens with waste PET flakes were elaborated.
- Effects of gamma radiation and waste PET flakes concentrations were studied.
- Improvement of 34% on the compressive strength was obtained.
- Elasticity modulus was improved up to 114% respect to control concrete.
- Structural changes on the waste PET flakes by gamma radiation were evaluated.

ARTICLE INFO

Article history:

Received 25 February 2020

Received in revised form 17 September 2020

Accepted 18 September 2020

Available online 7 October 2020

Keywords:

Polyethylene terephthalate

Waste

Recycling

Sustainability

Concrete

Gamma radiation

ABSTRACT

Severe environmental problems are generated by the excessive amount of waste Polyethylene Terephthalate (PET). A popular way to reuse it is to recycle as filler material in concrete technology. However, some mechanical properties decrease because of adhesion weakness between cement paste and waste polymers, when they are added. One alternative solution to deal with it is to use the radiation. In this respect, the influences of waste Polyethylene Terephthalate (PET) flakes and gamma radiation on strength, deformation capacity and elasticity modulus of cement based concrete were studied. In production, cement, water, gravel and sand were mixed. The sand was replaced with the PET flakes with 0.71, 1.4, 2.8 mm at 1, 2.5 and 5% in volume. Then, the specimens were subjected to 100, 150 and 200 kGy. Results present higher compressive strength (~34%) and elasticity modulus (~114%) for irradiated concretes when compared with those values obtained for reference specimen. However, deformation decreases about 88%. Such mechanical results were associated with the physicochemical characteristics induced by gamma rays on flakes and cement; which were evaluated by SEM, TGA, DSC and X-ray diffraction (XRD).

© 2020 Elsevier Ltd. All rights reserved.

1. Introduction

Polyethylene Terephthalate (PET) is preferred in beverage bottles. The PET after its short service-life becomes in a serious environmental problem due its non-biodegradability nature. And the PET bottles present a pollution effect including their final disposal and by-products generated during its production stage. Because

their degradation takes long time, an alternative is to incinerate them. However, by-products like chlorine gas and dioxins which are highly toxic are left to air. Fortunately for us, PET recycling is an emergent priority of governments around the world [1].

Recycling of PET bottles produces a variety of products, including fibers, flakes or particles; which are used as raw material instead of the mineral aggregates into cement based composites. Addition of PET to mortars or concrete produce changes on their mechanical properties. Such changes are highly sensitive to size, usage volume or fraction and shape of PET additive. For example:

* Corresponding author.

E-mail address: gonzomartinez02@yahoo.com.mx (G. Martínez-Barrera).

a) raising of the mechanical strength and the strain in addition more efficient crack-resistant are obtained, when adding low concentration of small-PET flakes. Nevertheless, the elasticity modulus values decrease for addition of large-PET flakes [2]; b) improvement on the flexural strength, up to 52%, as well as for compressive strength, up to 22.65%, were obtained when adding PET fiber (0.5–3.0% concentrations). However, workability of concrete decrease with increasing of PET fiber concentrations [3]; c) the flexural toughness and impact resistance increase when adding recycled PET fibers from bottles (0.05–0.30 vol%) with lengths of 10, 15 and 20 mm; however, no significant effects on properties such as compressive strength and elasticity modulus were observed, their rates reduce as fiber fraction increases [4]; d) notable increments on flexural strength and elasticity modulus were observed for polymer mortars with waste PET, from drink holders, as raw materials instead of virgin aggregates (5–20%). Moreover, the flexural and compressive toughness get improvement in addition to flexural and compressive strength when the PET fraction increases [5]; e) the ductility increases when adding a low content of recycled fiber from the PET bottles which are chopped. Fibers in the forms of lamellar shaped and “O”-shaped significantly increase toughness and also significantly affect post-cracking, such shapes help to stitch the cracked sections in the body of concrete [6]; f) the toughness is improved, while splitting tensile and flexural strength values are lightly large, but those for compressive strength significantly decrease, for concrete with PET flakes. Such behaviors are dependent on the three used PET shapes [7]; g) No notable effect on the strength and elasticity modulus were obtained, for cement mortars with PET fibers. However, I_5 , I_{10} , and I_{20} indexes declined with time because of degradation of fibers by alkaline hydrolysis in the body of concrete [8].

One alternative option for polymer recycling is the usage of ionizing radiation like gamma rays. It is well-known that ionizing radiation like gamma rays leads to both cross-linking and scission of polymer chains. Also crystalline structure is modified. When the degree of crystallinity increases the polymer gets a tougher, stiffer and harder than that for non-irradiated one. Moreover, whether cross-linking and scission form in the same fractions, or whether one or more controllers, relies on chemical composition of polymer [9].

In the case of polyethylene terephthalate (PET), gamma rays produce electrons in addition to the photons with low energy that are managing the alteration of its structure. At ~10 kGy, molecular changes are because of process of chain scission, caused by free radicals. Then, scission chains can be started again in order to produce cross-linking with contiguous molecules, which rise that no chemical degradation happens up to 200 kGy. For higher dose, at 900 kGy, up to 35% cross-linking of polymer chains is obtained, such change produces stability on its mechanical and physicochemical properties. Different results have been obtained in investigations concerning to PET irradiated with gamma rays, for example: a) it was possible to measure the radical stability against oxygen permeation as well as aromatic density of PET irradiated with gamma rays in an air atmosphere, by using EPR analysis [10]; b) the crystallinity degree in addition to activation energy improve. However, optical band gap (E_g) declines when the irradiation level is raised; which was corroborated by XRD and UV–vis spectroscopy [11]. A similar study was carried out for the PET from drink bottles, crystallinity increase (evaluated by XRD), yet direct and indirect band gap decrease, while the gamma rays rise [12]; c) improvements on the thermal stability were obtained for both raw and waste irradiated PET, according to the evaluation by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) [13]; d) in a similar study, improvements on the thermal stability and the dye dispersion in point of the intensity of color were obtained for the virgin and the waste PET as well

as blends of it. According to the evaluations by TGA, DSC and IR spectroscopy. In particular, 98% improvement on the dye skill with spread dye (in respect to the intensity of color), was obtained for the 80 virgin/20% waste PET mix irradiated at 50 kGy [13].

Information about the addition of PET to mortar or cement concrete for improvement of their strength characteristics like compressive, flexural and splitting tensile. Nevertheless, not too much information is reported about adding irradiated materials into concrete or to irradiate the concrete as a whole. The current studies of concrete with added polymers as fillers have focused mainly on the physicochemical evolution of the added polymers as well as on the structural deterioration of the concrete, as a whole or on their components [14]. Nevertheless, some studies involve gamma irradiation and modifications on the physical properties, for example: a) improvement of the compressive strength in cement paste by using irradiated recycled PET powder and fly-ash; which is possible because gamma rays increase the degree of crystallinity of recycled PET [15]. High compressive strength and diminution on the porosity and water absorption were obtained, when the irradiation level reaches from 10 kGy to 50 kGy for the mortar containing white sand and styrene-acrylic ester (SAE) (10 wt%) [16].

Alternative studies have contemplated influences of gamma ray and lead on concrete. Ionizing radiation produces improvement on the strength during solidification of the concrete, because gamma rays removed the micropores. Moreover, produced concretes with or without sand were subjected to gamma rays. Findings show that there were the increments up to 76% of the strength for irradiated concrete with sand, and 66% for those without sand [17]. Thus, physicochemical characteristics of mineral aggregates may be changed by gamma radiation. For instance, the carbonated samples increase their bending strength values when they are submitted to gamma irradiation. Moreover, irradiation causes that calcium carbonate polymorph near the calcium silica hydrate (C-S-H). It results in the filling characteristic pores. Such formation allows that the ordinary structure of carbonate be maintained [18].

Due to scarce knowledge about the usage of the ionizing radiation and waste polymers for development of strength characteristics cement based composites, in the present study, influences of gamma ray irradiations and waste PET flakes (from drink holders), on strength, deformation capacity and elasticity modulus properties of cement based mixtures were investigated. Different PET flake sizes (0.71, 1.4 and 2.8 mm) at different concentrations (1.0, 2.5 and 5.0 vol%), were evaluated, as well as irradiated doses of 100, 150 and 200 kGy.

2. Materials and methods

2.1. Mixture designs and production

It was Portland cement CPC-30R used as binder. Granulometry of sand in Table 1 and Granulometry of gravel in Table 2 are presented according to the ASTM sieve charts. Both mineral aggregates were obtained from a local company, located at Calimaya, Mexico. Cement concrete specimens (10 cm-long and 5 cm-diameter) were manufactured. The mixture proportions were presented in 3.

In the mix composition of the specimens, the cement/aggregate ratio was 1/2.75. Water/cement ratio was 0.485. The specific gravity of cement as 3.15 g/cm³, gravel as 2.67 g/cm³ and silica sand as 2.55 g/cm³ were specified according to ASTM C-305 standard.

PET flakes were obtained from the body of the waste beverage bottles in order to achieve a homogeneous size. Is to say, neither finish-shoulder part of the top nor heel-base on the bottom were not used. The first prepared size of 50 × 5 mm in average, while

Table 1
Size of the sand (Fineness modulus = 1.59).

Mesh	Size (μm)	Retained weight (g)	Retained weight (%)	Retained accumulated weight (%)
30	600	79.0	29.0	29.0
50	300	74.9	27.0	56.0
100	150	52.4	19.0	75.0
200	75	36.9	13.0	88.0
Bottom tray	Bottom tray	33.7	12.0	100.0

Table 2
Size of the gravel.

Mesh	Size (μm)	Retained weight (g)	Retained weight (%)	Retained accumulated weight (%)
3/8	9.5	20.3	2.0	2.0
4	4.75	902.8	91.0	93.0
8	2.36	57.8	6.0	99.0
Bottom tray	Bottom tray	7.0	1.0	100.0

second one shortened them five times (10×1 mm). After, the obtained flakes were subjected to the mechanical cutting process for 1 h. Finally, they were sieved during 50 min, for to obtain sizes of 0.71 mm, 1.4 mm and 2.8 mm. The objective was to have a size ratio of 1:2:3 between them, for a better distribution of them into concrete mix.

For producing cement concrete specimens with waste PET flakes, silica sand was partially replaced with 1.0, 2.5 and 5.0 vol % of waste PET flakes. Thus, three sizes and three concentrations of PET flakes were used. For each size and concentration of PET flakes five concrete specimens were elaborated. The quantities of each component of the cement concrete with waste PET flakes are shown in the Table 3. Now, the total volume of the cement concrete considers the specific gravity of PET (1.45 g/cm^3).

Finally, after curing for 24 h, concretes were left to the curing room with 23.0 ± 2.0 °C according to ASTM C/192 M-00 and 95% of relative humidity and their surface exposed to moisture, according to ASTM C-51.

2.2. Gamma irradiation procedure

Concretes with waste PET flakes cured at 28 days, were irradiated at doses of 100, 150 and 200 kGy. The dose rate was applied as 3 kGy/h in a gamma irradiator Transelektro™LGI-01 IZOTOP with pencils of ^{60}Co at the National Institute of Nuclear Research Mexico (ININ).

2.3. Morphology and mechanical testing

Surface morphology of non-irradiated and irradiated concrete specimens were investigated by SEM. SEM device (JSM-6510LV) has max resolution of 5 nm and an acceleration voltage 30 kV in secondary electron mode. Compressive strength tests were done by using Universal Testing Machine model 70-S17C2 (Controls™, Cernusco, Italy) in accordance with ASTM C-39 M-01. Testing tolerance was 28 days \pm 20 h according to ASTM C39/C39M-14.

Table 3
Quantities of each component of the concrete with waste PET flakes.

Component	PET (g)		
	1.0%	2.5%	5.0%
Portland cement	420	420	420
Water	413	413	413
Gravel	1,152	1,152	1,152
Silica Sand	914.70	909.80	901.60
PET	3.26	8.17	16.33

2.4. Morphology and crystallinity of cement

The surface morphologies of both non-irradiated and irradiated cements were also investigated by SEM by using the same electronic microscope mentioned in the section 2.3. The XRD is a typical technique that is utilized to clarify the phases in the crystalline material. In this work, both amorphous and crystalline structure of cement may take role to get a decision about the mechanical behavior of the concrete. Crystallinity was clarified by XRD with Cu-K α radiation detector at 35 kV voltage and 30 mA current.

2.5. Morphology, chemical structure and thermal analysis PET flakes

Surface morphologies of both non-irradiated and irradiated PET flakes were investigated by the same electronic microscope mentioned in the section 2.3. Their chemical structure analyzes were analyzed by Raman spectroscopy in a spectrophotometer Shimadzu-IR Prestige-21. The PET flakes were recorded between 3800 and 800 cm^{-1} range, with resolution of 8 cm^{-1} and 32 scans. While, the thermal analysis was done by DSC, Perkin Elmer DSC-6. In testing, nitrogen gas (30 °C–450 °C) was used. The heating rate was 10 °C/min. Finally, TGA (Perkin Elmer TGA-7) investigations were fulfilled. It was surrounded at (30 °C –450 °C) and subjected to heating regime 10 °C/min under nitrogen media.

3. Experimental results and discussion

3.1. Compressive strengths of concretes

Compressive strengths of concrete specimens were given in Fig. 1. For clarifying the behavior of the concrete specimens when compared to the control one that does not contain the waste PET flakes and is not irradiated, the horizontal strip was add beginning from value of the control specimen. Experimental observations are evaluated in respect to three factors: I) radiation dose, II) PET flakes size, and III) PET flakes concentration.

For non-irradiated concrete specimens, the strength variation is from 12.6 MPa to 23.1 MPa. That are less than that of the control which has 26.7 MPa. a) Considering the size of waste PET flakes, the strengths decrease gradually while increasing the size of PET flakes. They have a reduction up to 52% respect to the control one. In particular, the strengths of concretes containing 0.71 mm PET were 83% higher than those with 2.8 mm PET; b) considering the concentration of waste PET flakes, values had maximum value when using 2.5 vol% of PET.

Compressive strengths of concretes which were not subjected to gamma radiation were highly related to the size and concentra-

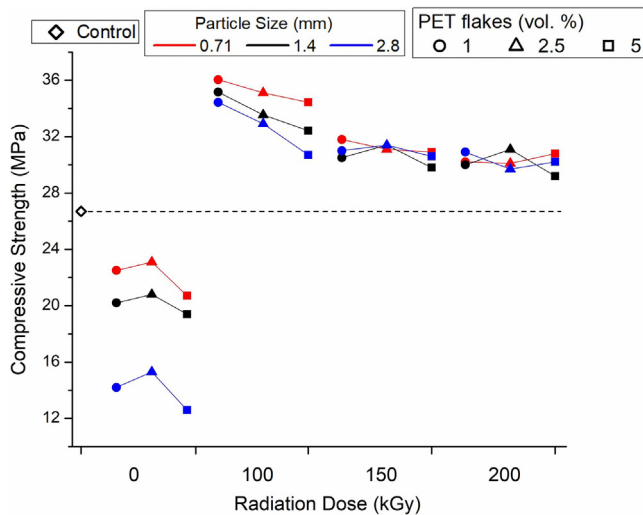


Fig. 1. Variations of compressive strength.

tion of PET flakes. Such behaviors may be attributed to the morphology observed for fractured concrete after compression test, as it is shown in Fig. 2. Regarding to PET particle size, for concrete with small PET flakes (0.71 mm), homogeneous surfaces with compact areas are observed. As it is known, small particle sizes have lower surface area compared to the large ones, thus compressive strength values increase. Nevertheless, with medium size PET (1.4 mm), the surfaces show detached particles (indicated by a circle), and some cracks (indicated by arrows), which produce decrease on the values of strength. Detrimental values were observed when the size of the PET (2.8 mm) was used. The surfaces are roughness with pronounced cracks (indicated by arrows), and cement does not surround some PET particles.

In the case of irradiated concrete: all strengths were higher than that the control specimen. The values ranging from 29.8 MPa to 36.0 MPa, the highest means a maximal improvement of 34%, which was acquired for concrete containing 1% of 0.71 mm waste PET flakes and subjection of 100 kGy. According to the parameters: a) Respect to the PET sizes, the values have a well-defined behavior at 100 kGy, and they decrease progressively when PET size increase. But at higher dose, they have variations between them. Nevertheless, their values have minimal differences. Finally, b) respect to the PET concentration, the values have a well-defined behavior at 100 kGy, they decrease progressively when increasing waste PET concentration. Nevertheless, at higher doses, minimal differences are obtained on the values.

Improvements on strength of concrete are because of the gamma irradiation influences on concrete components as well as on the PET flakes. As it is known, PET is a semi-crystalline polyester with microstructural isotropic properties and both glassy and

amorphous morphologies. When this is irradiated with gamma rays, scissions on their polymer chains are produced, generating decrease on the molecular weight, in addition to allow more molecular mobility and arrangement of its molecular structural, such changes promote increase on its crystallinity. Then, several of their mechanical properties are modified, for example, the elasticity modulus, toughness, stiffness, strength and hardness. Such modifications contribute to develop the bond between PET flakes and cement paste, thus improvement on the compressive strength is obtained.

3.2. Strain behaviors of concrete specimens

The strain values of all specimens studied at 28 days are shown in Fig. 3. For the concretes which were not irradiated, the strain values were in the range of 0.003–0.006 mm/mm. This last with the same value observed on the control concrete. With exception of the value for concrete specimen containing 1% of PET flakes in 0.71 mm size, all concrete specimens present less strain performance than that of the control specimen. According to the parameters: a) for the PET flake size, the values decrease progressively when increasing PET size, having a diminution up to 50%; b) respect to the PET flakes concentration, the values had the highest values when adding 1.0 vol% of PET.

In the case of concrete with gamma radiation subjection: all compressive strain capacities are less than that of control specimen and non-irradiated ones. Values obtained is in the range of 0.0007–0.0032 mm/mm. The lowest strains were observed on the concrete specimen which was subjected to 200 kGy gamma radiation. That presents a diminution of 88% when compared to the control one. According to parameters: a) for the PET sizes, the values have a well-defined behavior at 100 and 150 kGy, they increase progressively when the PET size increase too. Yet, at 200 kGy, the higher strain capacities were observed on the concrete containing PET with 1.4 mm size. Finally, b) respect to PET fraction, a well-defined characteristic is observed, the values increase progressively when increasing PET concentration.

Diminution on the strain capacities are because of the irradiation influences raised on both PET flakes and matrix. In the case of the PET flakes, irradiation cause scission of polymer chains, higher crystallinity and surface modifications. Such changes generate more contact points between PET flakes and the concrete components, as it is shown in Fig. 4, for the fracture zone of concrete with lowest compressive strain values (concrete with 0.71 mm PET size and irradiated at 200 kGy). At the lowest PET flakes concentration, 1.0%, a compact surface with hydrated cement areas is obtained, is to say, PET flakes are bonding with the hydrated cement paste, in consequence a more ductile concrete is produced than that control concrete. More added PET flakes, produces a less compact surface with less hydrated areas (indicated by arrows), thus compressive strain values decrease.

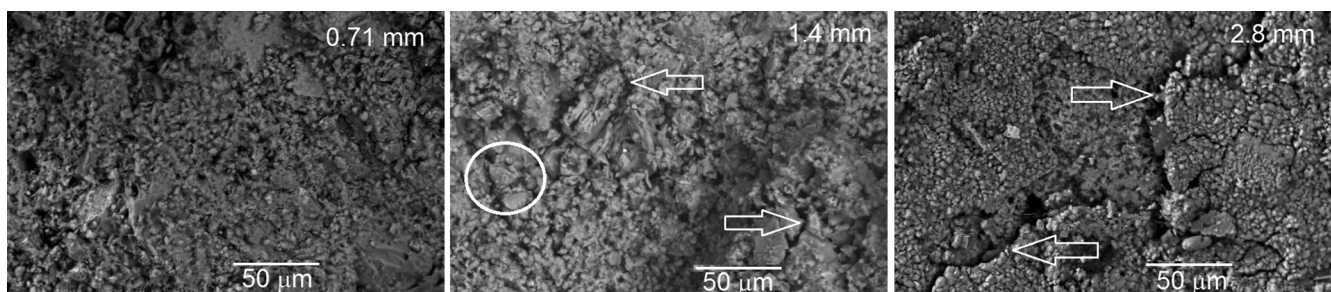


Fig. 2. Microstructures of non-irradiated specimens with different size of PET flakes.

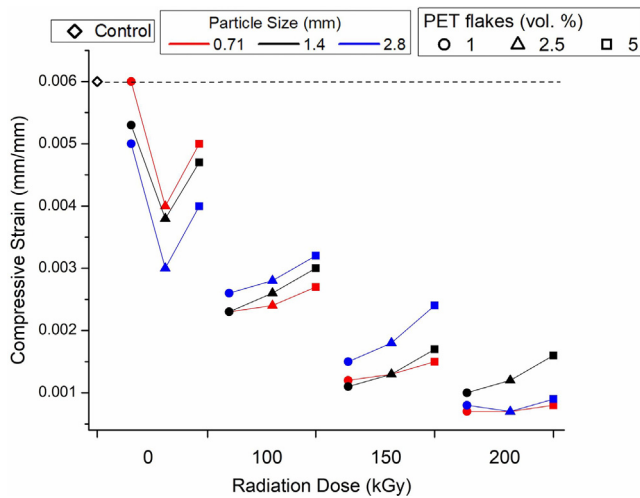


Fig. 3. Compressive strain capacities of the concrete specimens.

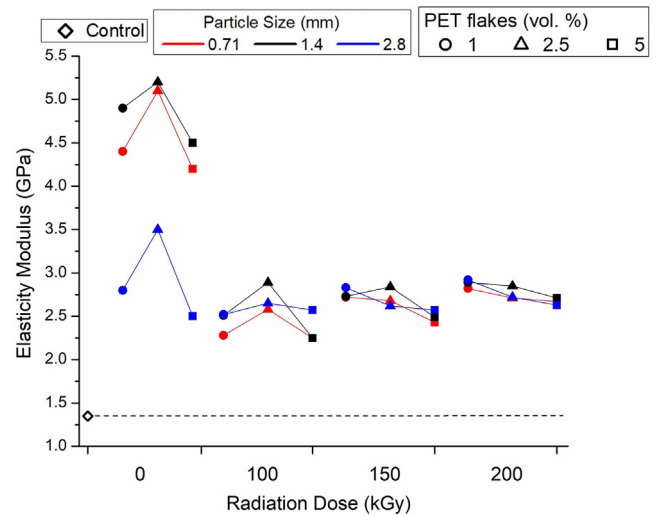


Fig. 5. Elasticity modulus of concretes.

3.3. Elasticity modulus of concretes

Elasticity modulus of specimens were presented in Fig. 5. For non-irradiated concrete specimens, values ranging from 2.5 to 5.2GPa, which are bigger than that of the control one with 1.3 GPa. According to the parameters: a) for PET flakes sizes, the highest modulus was observed as 5.2 GPa on specimen containing PET flakes with 1.4 mm size. That presents increment of 285% when compared to the control one; b) according to PET flakes concentration, the highest modulus was observed on specimens containing 2.5% PET flakes. So, to produce hardest concrete, the appropriate mix contains 2.5% PET with 0.71 mm size.

When looked at the irradiated concrete, the elasticity modulus was higher than that of the control one. Values ranging from 2.2 to 2.8 GPa. The highest elasticity modulus was observed on the concrete specimen containing 2.5% of PET flakes with 1.4 mm and irradiation of 100 kGy, namely 2.8 GPa. That presents a maximal increment of 114%. According to the parameters: a) for PET sizes, the highest one was observed on specimen containing PET size with 1.4 mm size. The lowest with 0.71 mm PET size; while b) respect to the PET concentration, the highest one was observed on specimen containing 2.5% PET flakes.

It is notable, that irradiated concretes at 150 and 200 kGy have minimal differences between them, is to say, around 114% improvement for elasticity modulus can be kept when dose 150 or 200 kGy are applied, independently of the particle size and concentrations of PET flakes. Moreover, such behavior is consequence of both effects scission and cross-linking cause by the irradiation on the PET flakes.

The increments in the strength and elasticity, as well as diminution on the deformation of the concrete specimens, may be associ-

ated with variations induced by the irradiation procedure on physicochemical properties of both cement and PET flakes, which are describe in the follow sections, according to the results observed by the analytical techniques.

3.4. Analysis of morphology and crystallinity of non-irradiated and irradiated cement

Gamma irradiation influences on irradiated cement were quantified by SEM as presented in Fig. 6. For non-irradiated cement particles, various particle sizes were observed, while for those subjected to 100 kGy and 150 kGy a more quantity of detached particles are observed. Finally, at 200 kGy less space between cement particles are observed, an in consequence a more compact surface is obtained, which is result of the ionizing radiation.

Assessment of crystallinity of cement particles was provided. Spectra for non-irradiated and irradiated cement were presented in Fig. 7. Data were obtained between 5° and 55° (2θ). The pattern presents six main peaks at 2θ = 29.4° corresponding to alite (monoclinic) (Ca3SiO5); at 32.2° for ferrite (Ca2(AlxFe1-x)2O5); at 32.6° and 34.3° for aluminat (Ca3Al2O6); at 41.3° for periclase (MgO), and at 51.7° for alite (Ca3SiO5). The alite is associated with the crystallographic planes (101), while ferrite to planes (100) and aluminat to (023) planes.

The crystalline alignment was kept in cement after subjection to gamma radiation since peaks were placed in the same standing (2θ degree) than those of ones which were not subjected to irradiation. However, the degree of crystallinity decrease or increase depending of the choose peak. In Fig. 8 are shown the changes for the intensity for each peak.

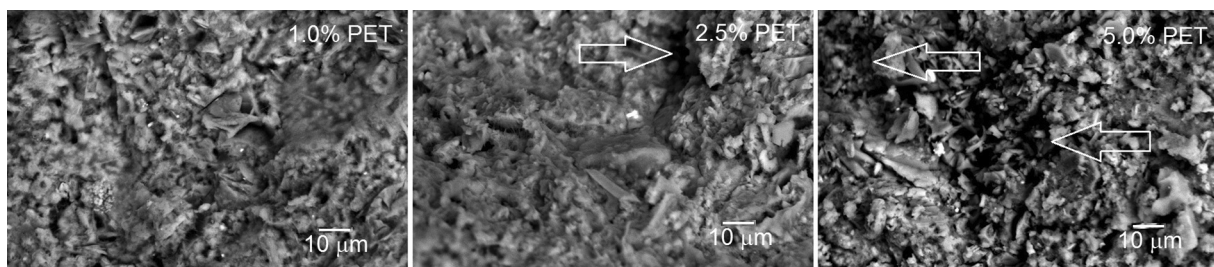


Fig. 4. SEM images of concrete with 0.71 mm PET size and irradiated at 200 kGy.

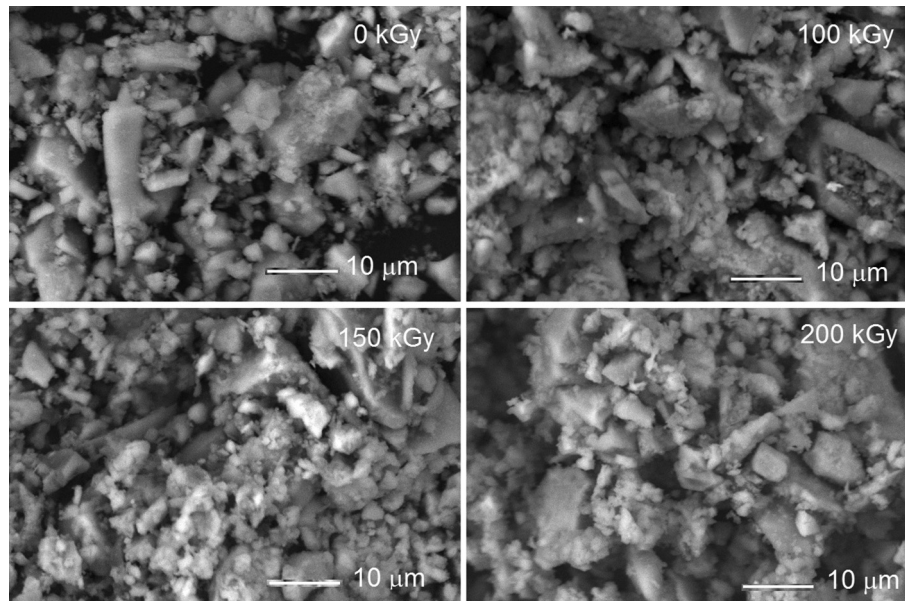


Fig. 6. Microstructure views of cement.

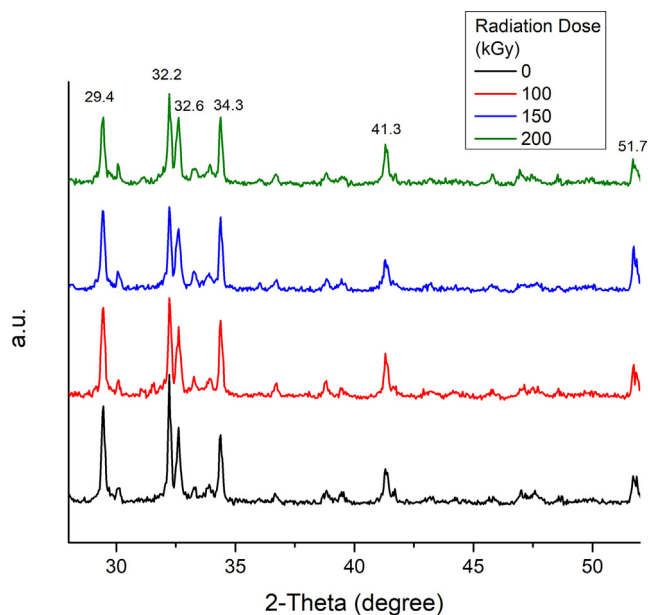


Fig. 7. XRD pattern of the cement.

For four peaks the crystallinity decreases according to the irradiation dose increases, at $2\theta = 32.2^\circ$, 29.4° , 34.3° and 32.6° , corresponding to ferrite, alite and aluminate. The most intense peaks are for ferrite (32.2°) and alite (29.4°), whose intensity values diminished up to 28% and 29%, respectively, when cement was irradiated at 200 kGy. The other two peaks that decreased, corresponding to aluminate, had minimal differences on their intensities according to the irradiation doses. In the contrary case, the less intense peaks at 41.3° and 51.7° corresponding to periclase and alite had lightly increments according to irradiation dose increase. Both crystallinity behaviors in the cement (increment and diminution), contribute for having higher compressive strength and elasticity modulus as well as lower strain values for irradiated concretes.

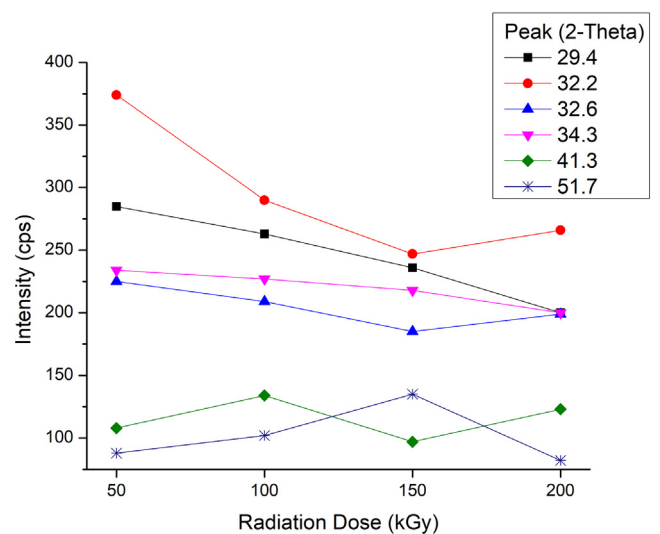


Fig. 8. The intensities for each diffraction peak of concretes.

3.5. Analysis of the morphology, chemical structure and thermal behavior of non-irradiated and irradiated PET flakes

Mechanical properties of concrete specimens are associated with changes in the microstructure of the waste PET flakes after irradiation as seen from Fig. 9. Smooth surface on the non-irradiated PET was observed. The deterioration on the surface starts when the gamma radiation was used. Some lines appear at 100 kGy. Nevertheless, at 150 kGy the rough surface is obtained, with the unbounded particles (indicated by circles) and some cavities (by arrows). Above 200 kGy, rougher surface structure with the unbounded particles (indicated by circles) and well-defined lines (by arrows) was observed.

Changes on the morphology were result of interrupting of the polymer chains of the waste PET. On the PET surfaces more touching places are formed. So higher superficial areas are developed. Thus, these altered PET flakes connecting to surfaces of hydrated

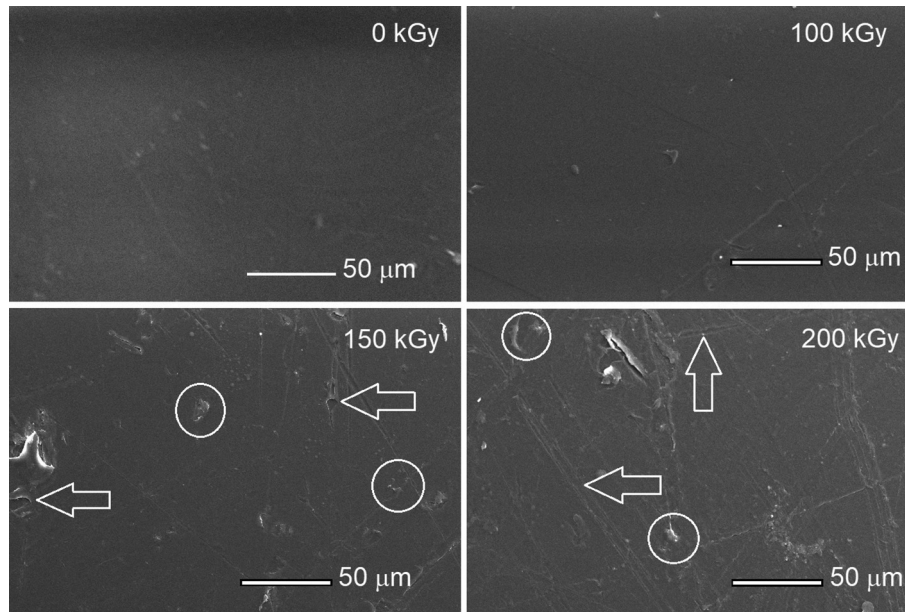


Fig. 9. Microstructures of waste PET flakes.

paste (included cement and mineral aggregates), and to improve the strength and elasticity modulus.

Respect to chemical structure of the PET flakes, analyzed by Raman spectroscopy, in Fig. 10 several bands are shown. The most intense sets were placed at 1618 cm^{-1} that was corresponding to the C = C ring increasing vibrations. Other less intense band is located at 1731 cm^{-1} related to the C = O mode. This carbonyl band combined with the C-O-C ester bands at 1293 cm^{-1} represents the features of the terephthalate ester. Finally, a band attributed to the CH₂ groups in the O-CH₂CH₂-O- sequence, is located at 863 cm^{-1} . Intensities and frequencies of these CH₂-related bands are frequently discussed in terms of the *trans*- and *gauche*-rotational isomers of the O-CH₂CH₂O- groups, related with the crystallinity and orientation of polymer chains of PET.

As it is shown in Fig. 11, the intensity of each band gradually decreases according to the irradiation dose increases. Such inten-

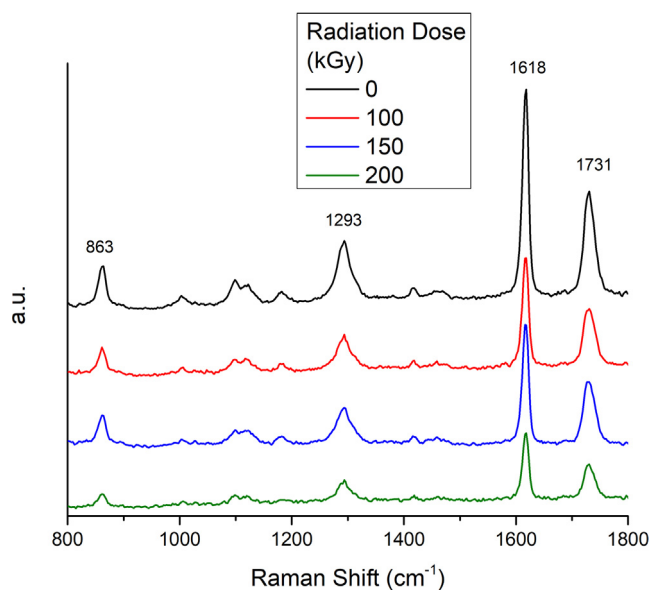


Fig. 10. Raman spectra of waste PET flakes.

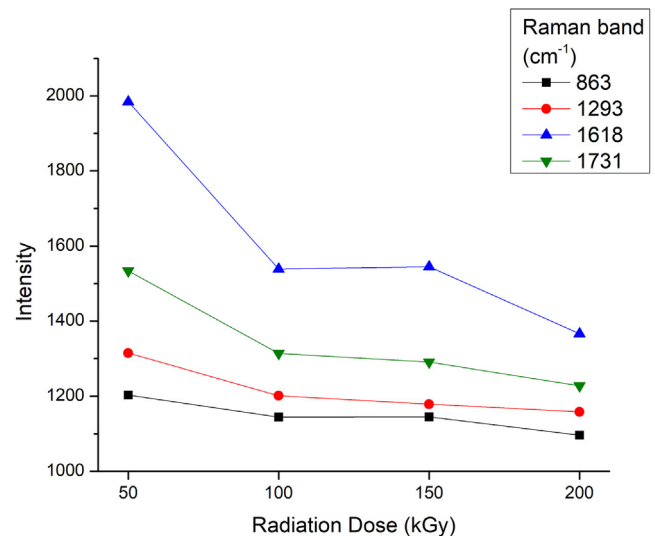


Fig. 11. Raman bands intensities of waste PET flakes.

sity diminutions mean lower degree of crystallinity and they also are related with the orientation of polymer chains of PET. The highest diminution, 31.1%, is obtained for PET irradiated at 200 kGy, which correspond to the most intense band with at 1618 cm^{-1} that is associated with C = C ring stretching vibrations. While 19.8% of reduction, is obtained the band for 1731 cm^{-1} that is corresponding carbonyl stretching vibration. Other bands (1293 cm^{-1} and 863 cm^{-1}) have intensity reductions of 11.9% and 8.8%, respectively.

For to know which of the two behaviors happen, scission or cross-linking of polymer chains in PET flakes after irradiation, the thermal analysis is adequate for such purpose. In Fig. 12, the thermogravimetric curves of both waste PET flakes were presented. The waste PET is a hydrophobic polymer. So the water cannot present on its surface. For non-irradiated PET flakes the mass loss at the start of degradation T_{0.5} (5% of mass loss), is located at 425.7 °C . Such temperature decreases 7.2 °C at 150 kGy of irradiation dose, but increases 15.3 °C at 200 kGy, in regards of the tem-

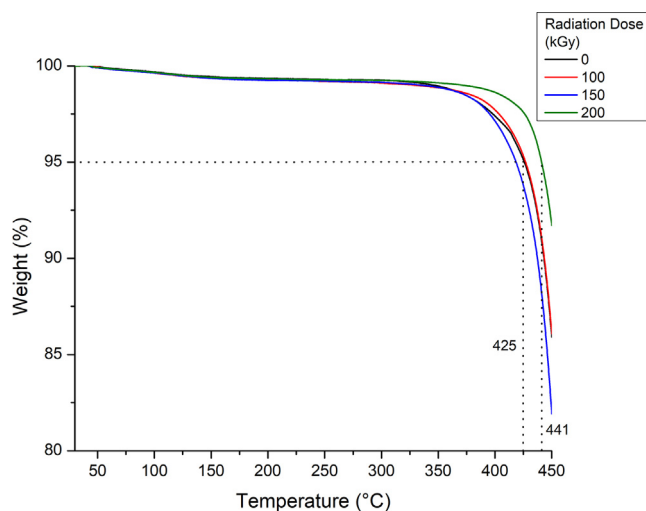


Fig. 12. TGA curves of the waste PET flakes.

perature for PET which was not irradiated. Thus, temperature diminution at 150 kGy is associated with the polymer chain scissions. Then less heat is necessary for beginning of degradation. Although, cross-linking is obtained at 200 kGy, thus more heat is necessary for its disintegration.

In case of the DSC analysis, the curves of both waste PET flakes, irradiated and not, are presented in Fig. 13. It is possible to evaluate crystallinity and degradation according to temperature increase. As it is known PET is a thermoplastic polymer that has a semi-crystalline structure. In the DSC thermograms, non-irradiated PET flakes show degradation at 243.5 °C, corresponding to melting temperature (T_m , an endothermic peak). For irradiated PET, such degradation temperature has a lightly increment up to 6 °C as well as an improvement of 12% on the heat flow, is to say more energy is required for degradation of the PET flakes.

Following the DSC curves, other endothermic peak occurred at 442 °C for non-irradiated PET flakes, such temperature is almost constant for irradiated PET flakes, with minimal variations around 3 °C. Nevertheless, the irradiated PET flakes show increase up to 30% on the heat flow. Thus, gamma radiation produces cross-

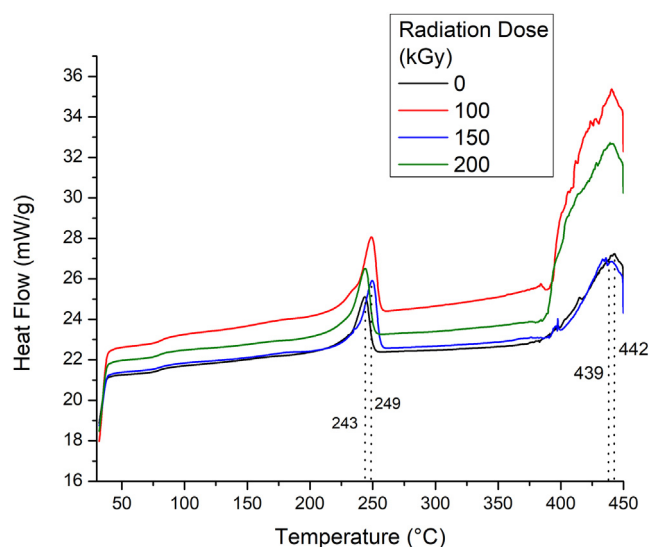


Fig. 13. DSC curves of the waste PET flakes.

linking of the chains, which needs more energy for their degradation.

4. Conclusions

The waste PET flakes and gamma radiation are sufficient options in order to increase the mechanical performance of cement based concrete. Moreover, gamma radiation may be a useful application and method in point of the recycling of the waste PET. According to the results, all irradiated concrete specimens have much strength and elasticity modulus than that of the control specimen, namely up to 34% and 114%, respectively. Nevertheless, in regards of the strain capacity, all irradiated specimens have an opposite behavior, they are less values than that of the control specimens, namely up to 88%. They increase progressively when increasing PET concentration. Such mechanical characteristics are bond with the alterations induced by irradiation on physicochemical properties of both cement and PET flakes. The compressive strength values of concretes subjected to gamma radiation were less than that of the control concrete, they decrease progressively when increasing PET size and have a maximum value when adding 2.5% PET flakes. Moreover, the compressive strain values of all concrete specimens have less strain capacity than that of the control specimen, they decrease progressively when increasing PET size. Not so for elasticity modulus, which are higher.

CRediT authorship contribution statement

Gonzalo Martínez-Barrera: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. **Liliana Ávila-Córdoba:** Methodology, Validation. **Fernando Ureña-Núñez:** Investigation. **Mar Alonso Martínez:** Formal analysis. **Felipe Pedro Álvarez Rabanal:** Validation, Writing - review & editing. **Osman Gencel:** Investigation, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Financial support for one of the authors (G. Martínez-Barrera), through Sabbatical Year by National Council for Science and Technology of Mexico (CONACYT), and the Autonomous University of the State of Mexico (UAEM) is acknowledged.

References

- [1] A.B. Raheem, Z.Z. Noor, A. Hassan, M.K.A. Hamid, S.A. Samsudin, A.H. Sabeen, Current developments in chemical recycling of post-consumer polyethylene terephthalate wastes for new materials production: a review, *J. Clean. Prod.* 225 (2019) 1052–1064, <https://doi.org/10.1016/j.jclepro.2019.04.019>.
- [2] L. Ávila Córdoba, G. Martínez-Barrera, C. Barrera Díaz, F. Ureña Nuñez, A. Loza Yañez, Effects on mechanical properties of recycled pet in cement-based composites, *Int. J. Polymer Sci.* 2013 (2013) 1–6, <https://doi.org/10.1155/2013/763276>.
- [3] J.M. Pandya, B.M. Purohit, Experimental study on the mechanical properties of concrete incorporating PET fibers, *Int. J. Sci. Res. Dev.* 2 (9) (2014) 43–45.
- [4] F. Pelisser, O.R.K. Montedo, P.J.P. Gleize, H.R. Roman, Mechanical properties of recycled PET fibers in concrete, *Mater. Res.* 15 (2012) 679–686. <https://doi.org/10.1590/S1516-14392012005000088>
- [5] J.M.L. Reis, E.P. Carneiro, Evaluation of PET waste aggregates in polymer mortars, *Constr. Build. Mater.* 27 (1) (2012) 107–111, <https://doi.org/10.1016/j.conbuildmat.2011.08.020>.
- [6] D. Foti, Preliminary analysis of concrete reinforced with waste bottles PET fibers, *Constr. Build. Mater.* 25 (4) (2011) 1906–1915, <https://doi.org/10.1016/j.conbuildmat.2010.11.066>.

- [7] N. Saikia, J. De Brito, Waste Polyethylene Terephthalate as an aggregate in concrete, *Mater. Res.* 16 (2013) 341–350, <https://doi.org/10.1590/S1516-14392013005000017>.
- [8] D.A. Silva, A.M. Betioli, P.J.P. Gleize, H.R. Roman, L.A. Gómez, J.L.D. Ribeiro, Degradation of recycled PET fibers in Portland cement-based materials, *Cem. Concr. Res.* 35 (9) (2005) 1741–1746, <https://doi.org/10.1016/j.cemconres.2004.10.040>.
- [9] G. Burillo, R.L. Clough, T. Czikovszky, O. Guven, A. Le Moel, W. Liu, A. Singh, J. Yang, T. Zaharescu, Polymer recycling: potential application of radiation technology, *Radiat. Phys. Chem.* 64 (1) (2002) 41–51, [https://doi.org/10.1016/S0969-806X\(01\)00443-1](https://doi.org/10.1016/S0969-806X(01)00443-1).
- [10] M. Mariani, U. Ravasio, G. Consolati, A. Buttafava, M. Giola, A. Faucitano, Gamma irradiation of PolyEthyleneTerephthalate and PolyEthyleneNaphthalate, *Nucl. Instrum. Methods Phys. Res., Sect. B* 265 (1) (2007) 245–250, <https://doi.org/10.1016/j.nimb.2007.08.054>.
- [11] S. Siddhartha, K. Aarya, S.K. Dev, J.B.M.K. Raghuvanshi, M.A. Wahab, Effect of gamma radiation on the structural and optical properties of Polyethylene terephthalate (PET) polymer, *Radiat. Phys. Chem.* 81 (4) (2012) 458–462, <https://doi.org/10.1016/j.radphyschem.2012.06.046>.
- [12] V. Kumar, Y. Ali, R.G. Sonkawade, A.S. Dhaliwal, Effect of gamma irradiation on the properties of plastic bottle sheet, *Nucl. Instrum. Methods Phys. Res., Sect. B* 287 (2012) 10–14, <https://doi.org/10.1016/j.nimb.2012.07.007>.
- [13] T.M.A. Razek, H.M. Said, M.R. Khafaga, A.W.M. El-Naggar, Effect of gamma irradiation on the thermal and dyeing properties of blends based on waste Poly(ethylene terephthalate) blends, *J. Appl. Polym. Sci.* 117 (2010) 3482–3490, <https://doi.org/10.1002/app.32217>.
- [14] A. Usman, M.H. Sutanto, M. Napiah, Y.F. Huang, K.W. Tan, L. Ling, K.H. Leong, Effect of recycled plastic in mortar and concrete and the application of gamma irradiation – a review, *E3S Web Conf.* 65 (2018) 05027, <https://doi.org/10.1051/e3sconf/20186505027>.
- [15] C.E. Schaefer, K. Kupwade-Patil, M. Ortega, C. Soriano, O. Büyükoztürk, A.E. White, M.P. Short, Irradiated recycled plastic as a concrete additive for improved chemo-mechanical properties and lower carbon footprint, *Waste Manage.* 71 (2018) 426–439, <https://doi.org/10.1016/j.wasman.2017.09.033>.
- [16] M.M. Khattab, Effect of gamma irradiation on polymer modified white sand cement mortar composites, *J. Ind. Eng. Chem.* 20 (1) (2014) 1–8, <https://doi.org/10.1016/j.jiec.2013.04.001>.
- [17] D. Rezaei Ochbelagh, S. AzimKhani, H. Gasemzadeh Mosavinejad, Effect of gamma and lead as an additive material on the resistance and strength of concrete, *Nucl. Eng. Des.* 241 (6) (2011) 2359–2363, <https://doi.org/10.1016/j.nucengdes.2011.03.001>.
- [18] I. Maruyama, S. Ishikawa, J. Yasukouchi, S. Sawada, R. Kurihara, M. Takizawa, O. Kontani, Impact of gamma-ray irradiation on hardened white Portland cement pastes exposed to atmosphere, *Cem. Concr. Res.* 108 (2018) 59–71, <https://doi.org/10.1016/j.cemconres.2018.03.005>.