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Case study

Waste tire rubber particles modified by gamma radiation and their use as modifiers of concrete

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A B S T R A C T

Nowadays the excessive amount of waste tire rubber generates serious environmental problems. One of the alternative ways for its recycling is as filler in cement concrete. Nevertheless, as it is known recycled materials added to cement concrete decrease certain mechanical properties due to the poor adhesion between fillers and cement matrix. For resolve this problem, ionizing radiation has been used. For these reasons, in this work, cement concrete specimens were produced with cement, water, rock crushed and sand; this last was partially substituted by particles of waste tire rubber. Then the compression properties of the specimens were evaluated following the experimental parameters: a) gamma irradiation dose (200, 250 and 300 kGy), b) particle size of tire rubber (0.85 and 2.8 mm), and c) particulate concentration of tire rubber (1, 3 and 5 wt. %). In addition, the mechanical compression results were related with the changes on the physicochemical properties of the irradiated tire particles, which were analyzed by Fourier Transform Infrared (FT-IR), Raman and UV–vis spectroscopies, as well as by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA) an Differential Scanning Calorimetry (DSC). The results show improvements on the: a) elasticity modulus, up to 161 %, for cement concrete with non-irradiated particles of tire rubber, and up to 108 % when adding irradiated ones, b) deformation, up to 21 %, when adding non-irradiated tire particles; and c) compressive strength up to 8 % when adding non-irradiated tire particles. Such improvements on the mechanical features were related with the physicochemical changes provoke by gamma rays on the waste tire particles. Such changes were evaluated by the mentioned analytic techniques.

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1. Introduction

Every year millions of waste automotive tires are produced, 75 % of them are thrown into landfills and illegal dumps, and the remainder go to cement manufacturers as alternative fuel; which is a current practice in many countries [1]. Environmental and social problems are generated by such final disposition as well as for the slow degradation of the tire rubbers. During the burning of tires in open places, there are not control on the emissions of aromatic hydrocarbons, nitrogen dioxide, sulfur dioxide, carbon monoxide and suspended particles. In consequence, the air quality and the human health are deteriorated. Moreover, concentration of waste tires in urban zones generate leachates, and together with the contaminants (aluminum, zinc, manganese, iron, cadmium, lead and organic compounds) contaminate soil, surface water and groundwater. In addition, due to its hydrophobic characteristic, the waste tires thrown into illegal dumps hold water and becoming breeding grounds for disease-carrying mosquitoes [2].

Applications of waste tires in asphalt pavements have been effective, but not enough for reducing their quantity in landfills and illegal dumps. Nevertheless, an alternative is to use them as partial substitute of fine or coarse aggregates in cement concrete. According to the published works, rubberized concrete shows improved properties, for example: a) high resistance to freeze-thaw, acid attack and chloride ion penetration. In addition, silica fume enables to achieve high strength and high resistance to sulfate, acid and chloride environments [1], b) durability properties, water absorption and permeability increase with increasing crumb rubber concentrations, for cement concrete specimens with crumb rubber (up to 5.5 wt. %), as a substitute of fine aggregates. Nevertheless, the workability, compressive and flexural strength decreases with increasing crumb rubber concentrations. Moreover, the abrasion resistance also decreases due to low adhesion between crumb rubber and cement paste [3], c) the abrasion resistance increases with increasing tire rubber concentration, for concrete with replacing up to 20 % of fine aggregates by tire rubber particles (0.6–4.0 mm). High abrasion resistance can ensure applications where abrasive forces between surfaces and moving objects are present, for example, in pavements, floors and concrete highways [4].

In other studies, d) the freeze-thaw resistance of concrete increases, up to 89 %, when crumb rubber concentration increase (5–20 %), which replacing sand. Nevertheless, some properties decrease, as the compressive strength values (up to 68 %), the ultrasonic pulse velocity and the capillary-wall thickness and the pores space [5], e) improvements on the abrasion resistance and water absorption, not so for compressive strength, flexural tensile strength, pull-off strength and depth of water penetration, for high strength cement concrete with scrap tire rubber, replacing the natural fine aggregates (up to 20 %). In particular, the crumb rubber may be used up to 12.5 wt. % for obtaining strength above 60 MPa, or to use 2.5–7.5 % crumb rubber for diminution on the depth of chloride penetration, have little loss of the weight and compressive strength after acid attack [6,7].

In the case of self-compacting rubberized concrete (SCRC): f) highest compressive and tensile strength values were obtained for concrete with different concentrations of crumb rubber (10–40 %) and different size (2, 5 and 10 mm) [8]; g) the deformation and energy absorption increase, not so for workability and mechanical properties, for concrete with crumb rubber (10–40 %), heating from 100 °C to 600 °C. The fine aggregates were replaced with 2–5 mm crumb rubber particles, and coarse aggregates by 5–10 mm crumb rubber [9].

Combination of waste rubber and polymers have been used as fillers into cement concrete, for example: a) waste crumb rubber (15 wt. %) and polyethylene terephthalate (PET) (5, 10 or 15 wt. %) with 9 mm size, for producing sustainable and ecologically safe concrete submitted to acidic environment. The results show highest resistance when adding PET or PET and crumb rubber particles, after 60-day sulfuric acid exposure [10], b) crumb rubber (CR) and steel fibers coated with rubber (FCR), were added (20–100 %), as substitutes of mineral aggregates. The results show diminution on the mechanical properties and thermal conductivity for high concentrations of CR and FCR. Moreover, concrete with FCR had higher mechanical values than that with CR [11].

There are a lot of information concerning to add tire rubber for improvement of the mechanical properties of cement concrete. Nevertheless, information concerning to add irradiated materials into concrete is very limited. Respect to the effects of gamma irradiation on the physicochemical properties of tire rubber, a lot of studies have been reported, but not so for its use as filler into concrete. Mainly, those studies related to natural rubber (NR) and styrene butadiene rubber (SBR). The latter is a mix of the styrene and butadiene monomers, which is polymerized either by solution or emulsion processes. The SBR have good abrasion resistance and aging stability when protected by additives. In a study, natural rubber and styrene butadiene rubber were irradiated from 50 kGy to 250 kGy. The results show improvement on the tensile strength and tensile modulus as well as high thermal stability. Nevertheless, the elongation at break decrease when gamma radiation dose increase. Such results are due to cross-linking and scission of the polymer chains caused by the irradiation process. In fact, higher values on the cross-linking density generate better thermal stability, as it is known, ionizing radiation cause thermal decomposition of vulcanizates and increase the density [12,13]. In other study, the tensile strength, hardness and gel content increase according to gamma radiation dose increase (up to 100 kGy), in mixtures of styrene-butadiene rubber (SBR) and waste tire rubber [14]. In the case of crumb rubber, it was irradiated at 300 kGy, shown ductility at low temperature, stability at high temperature and high anti-aging performance [15].

As it is known, there a lot of information concerning to heavy density concrete and its use as shielding against gamma rays, for example, it is known that the shielding efficiency and mechanical properties of the concrete depended on the concentrations and the type of coarse aggregates (magnetite, barite, goethite, serpentine) and fine aggregates (silica fume, fly ash, ground granulate blast-furnace slag) [16]. Nevertheless, little information about ionizing radiation applied to polymer modified concretes is reported in the literature. Such studies have focused mainly on physicochemical evolution due to the effects of radiolysis. The main effects are based on polymer cross-linking and deterioration in the structure of the concrete. The results after irradiation show that: a) the compressive strength values increase but total porosity and water absorption decrease, when gamma irradiation dose increase (10–50 kGy), for cement mortar with styene-acrylic ester (SAE) [17]; b) the compressive strength and the density values increase when mortar specimens are irradiated, respect to non-irradiate ones [18]; c) interphase bonding is improved, increase not only strength and durability but also thermal, abrasion and waterproofing properties [19]; the compressive strength and bulk density increase but the total porosity decrease in an opposite direction with increasing the gamma irradiation dose, for cement mortars with nano-calcined clay and polyvinyl alcohol (PVA). X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and thermogravimetric analysis studies (TGA) confirmed the results [20]; highest mechanical performances were obtained for cement mortars with nano-calcined clay (NCC) (5–10 %) and 8 % of styrene–acrylic ester (SAE) (2–15 %), irradiated from 10 to 50 kGy. Thermal and microstructural characterizations were made by TGA, XRD and SEM techniques [21]; compression strength test, total porosity and water absorption percentages were measured in cement mortar with white sand and 10 % styrene–acrylic ester. The results were confirmed by SEM and TGA studies [22]; In the case of the lightweight white-cement pastes, compressive strength and bulk density decreased while the total porosity percentage increased when adding polyurethane foam waste (10–40 %). Moreover, gradual improvement on the mechanical and physical properties are obtained when adding styrene–butadiene rubber latex and dose from 50 kGy to 200 kGy are applied. Characterization was carried out by TGA, SEM and XRD [23]; the compressive strength, total porosity, and the bulk densities decrease with increase the styrene–butadiene-rubber (SBR) latex content (2.5–20 %) in cement mortar. However, the compressive strength values increase when gamma irradiation dose increase (10–50 kGy). XRD, TGA, acid attack, and microstructure were measured [24].

2. Experimental

2.1. Design and manufacture of cement concrete with waste tire particles

Cement concrete was produced with Portland cement CPC-30R, silica sand, rock crushed, and water, according to ASTM C-305 standard. Sieve analyses of sand and rock crushed aggregates are shown in the Tables 1 and 2.

Water was used without any solid residue or organic material suspended, and absent of fats or oils. Cement concrete without waste tire rubber particles (WTR) was denominated as control concrete. While, in cement concrete with waste tire rubber particles, silica sand was gradually replacement by tire particles of 2.8 mm (mesh 7) and 0.85 mm (mesh 20).

The cement concrete mixtures are described in the Table 3. The water/cement ratio was kept constant at 0.65, and the tire particle concentrations were 1, 3, and 5 % by weight. For each concrete mixture, five specimens were casting in cylindrical molds of 50 mm diameter and 100 mm height. After, they were cured in controlled temperature room at $23.0 \pm 2.0\,^{\circ}C$ and 95 % of relative humidity, in accordance with ASTM C511 standard.

2.2. Irradiation and characterization of irradiated waste tire particles

Particles of waste tire rubber were irradiated with gamma rays at 200, 250 and 300 kGy, using an irradiator Transelektro LGI-01 IZOTOP with pencils of ^{60}Co, and a dose rate of 2.5 kGy/h, located at the National Institute of Nuclear Research Mexico (ININ). After that, the irradiated particles were mixing into cement concrete at concentrations of 1, 3 and 5 wt. %.

The morphological characterization was made using a scanning electron microscopy (SEM) JEOL-JSM-6510LV with a maximum resolution of 5.0 nm, and an acceleration voltage 30 kV.

As it is known, X-ray diffraction (XRD) is an analytical technique primarily used for phase identification of a crystalline material. The peaks in the spectrum can determine the positions of the atoms and provide information on unit cell dimensions. Moreover, amorphous or crystalline nature of the filler materials can be decisive on the mechanical properties of the concrete. In this work, crystallinity was evaluated by X-Ray Diffraction (XDR), using a Bruker Advance D8 diffractometer with a Linxeye detector, with Cu-Kα radiation at 35 kV voltage and 30 mA current.

Analysis of the chemical structure of the waste tire particles were carried out by three different spectroscopic techniques: a) Fourier Transform Infrared (FT-IR), in a scanning range of $4000-500\,cm^{-1}$, using a spectrophotometer SHIMADZU-IR Prestige-21; b) Ultraviolet visible spectroscopy (UV–vis), in a UV–vis spectrometer Perkin Elmer-Lambda-35, and c) Raman spectroscopy in a WITec Raman confocal microscope, in the $4000-500\,cm^{-1}$ range, with a 532 nm excitation wavelength.

Table 1
Sieve analysis of silica sand.

Mesh	Size (μm)	Retained weight (g)	Retained weight (%)	Retained accumulated weight (%)
30	600	186	28.88	28.88
60	250	155	24.07	52.95
100	150	178	27.64	80.59
200	75	73	11.34	91.93
Pan	Pan	52	8.07	100

Table 2
Sieve analysis of rock crushed.

Mesh	Size (mm)	Retained weight (g)	Retained weight (%)	Retained accumulated weight (%)
3/8 in	9.50	19.6	0.89	0.89
4	4.75	1005.3	45.66	46.55
8	2.36	611.7	27.78	74.33
16	1.18	345.3	15.68	90.01
60	0.25	127.5	5.79	95.80
Pan	Pan	92.5	4.20	100

Table 3
Concrete mix proportions.

Code	Cement concrete (g)	Water (g)	Rock Crushed (g)	Silica Sand (g)	Waste tire particles (g)	Waste tire particles (%)
C0	78.7	51.2	196.8	118.1	0	0
C-1WTR	78.7	51.2	196.8	116.9	1.2	1
C-3WTR	78.7	51.2	196.8	114.6	3.5	3
C-5WTR	78.7	51.2	196.8	112.2	5.9	5

Finally, thermal analysis of the waste tire particles were carried out by Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC); both performed from 30 °C to 450 °C at a heating rate of 10 °C/min, under nitrogen atmosphere, by using a Perkin Elmer TGA-7, and a Perkin Elmer DSC-6 equipment, respectively.

2.3. Mechanical tests of cement concrete specimens

Control concrete specimens cured at 7, 14 and 28 days, as well as concrete with irradiated tire rubber particles cured at 28 days were tested. Testing tolerance was 28 days ±20 h according to ASTM C39/C39M-14 standard. The evaluation of compressive strength and the elasticity modulus was carried out in a Universal testing machine Controls 047H4 (Milano, Italy), with capacity of 2000 kN. One of the main objectives was to obtain cement concrete cured at 28 days with a compressive strength value of 18.5 MPa, according to standard ACI 211.1 [25].

3. Results

3.1. Compressive strength

3.1.1. Compressive strength of concrete with or without waste tire particles

Compressive strength values of control concrete and those with waste tire rubber particles are shown in Fig. 1. Such values were analyzed in terms of the parameters: I) curing time, II) tire rubber particle size, and III) particulate concentration. According to curing time, I) compressive strength values increase as curing time increase. The highest compressive strength values were obtained at 28 days; in the case of control concrete it was 18.6 MPa. II) Respect to the particle size, the highest values were obtained when adding large size particles (2.80 mm, 7 Mesh). III) Regarding to particulate concentration, two-well defined behaviors were obtained: a) for concrete with large particles (2.8 mm), compressive strength values gradually decrease when the particulate concentration increase; b) but for concrete with small particles (0.85 mm), highest values are obtained with 3 % of particulate concentration.

The concrete specimens with 1 % of tire particles of 2.8 mm, cured at 28 days showed the highest compressive strength values, namely 20.2 MPa. Which is 8 % higher than that value for control concrete. Such improvement is due to combination of low particulate concentration and large particle sizes; with these conditions high water content is needed, thus high workability and fluidity are obtained. Nevertheless, for high particulate concentration the compressive strength values decrease.

3.1.2. Compressive strength of concrete with non-irradiated and irradiated waste tire particles

As it was seen in the previous section, the highest compressive strength values were obtained for concrete with 1 % of large tire particles and cured at 28 days. Then, such kind of concretes were used as reference for produce new concrete specimens, but now adding irradiated particles. In Fig. 2 are shown the compressive strength values of concrete cured at 28 days with non-irradiated and irradiated tire particles. The analysis was carried out in terms of the parameters: a) irradiation dose, b) tire particle size, and c) particulate concentration. Moreover, for a better understood between concrete specimens and the control concrete, we decided to put a dotted straight line starting from the control concrete value and show graphically the values above or below this.

I) Regarding to irradiation dose: a) concrete with non-irradiated tire particles have lower values than that for control concrete, except those with 1 % of large tire particles (2.8 mm); b) in the case of concrete with irradiated tire particles, the

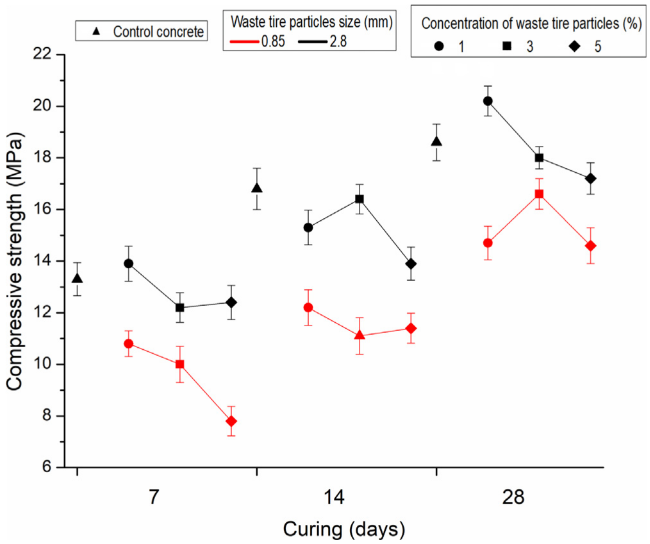

Fig. 1. Compressive strength of concrete at different curing time.

values have minimal difference among them; varying from 14.7 MPa to 17.4 MPa, which means values from 6 to 20 % lower than that for control concrete. Gamma rays (ionizing energy) generate cross-linking of polymer chains on the tire rubber, which restricts the movement of their molecules. Then, weak interfacial interactions are produced between cement matrix and the tire rubber particles, and in consequence strength values decrease.

II) Respect to particle size, higher compressive strength values are obtained when adding large size particles, which is more notable for concrete with non-irradiated tire particles. However, minimal differences on the values are obtained when adding irradiated particles, due to the physicochemical changes produced by gamma rays. Is to say, minimal difference on the values can be obtained independently of the particle size. III) Concerning to the particulate concentration, compressive strength values gradually decrease when the particulate concentration increase.

3.2. Compressive strain of concrete with non-irradiated and irradiated waste tire rubber particles

The compressive strain values of concrete cured at 28 days with non-irradiated and irradiated waste tire rubber particles are shown in Fig. 3. I) Respect to irradiation dose, two well-defined behaviors were obtained: a) the values for concrete with non-irradiated particles are higher than those with irradiated particles, this for concrete with large size particles. The value for control concrete was 0.0093 mm/mm, while for concrete with non-irradiated large size particles, the highest was 0.0117 mm/mm, which means 21 % higher. b) An opposite behavior was obtained for concrete with small size particles, the

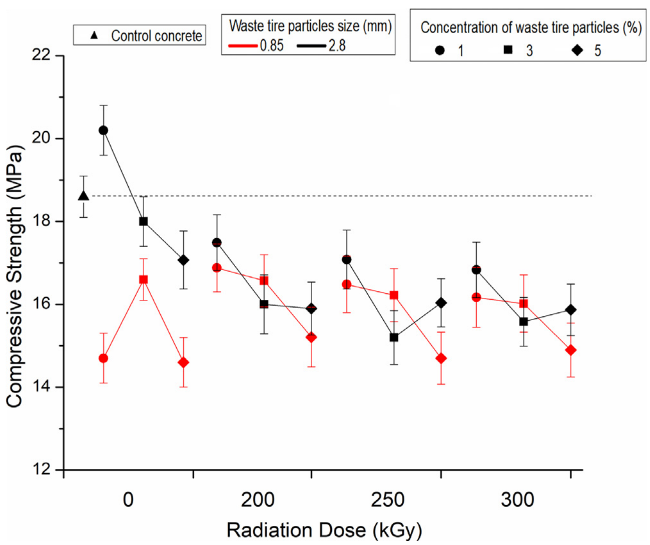

Fig. 2. Compressive strength of concrete with non-irradiated and irradiated waste tire rubber particles.

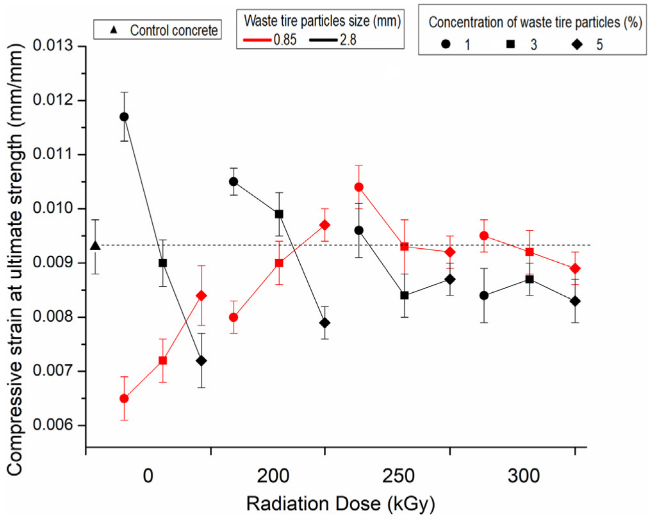

Fig. 3. Compressive strain of concrete with non-irradiated and irradiated waste tire rubber particles.

values for those with non-irradiated particles are lower than those with irradiated particles. An interesting behavior is obtained for concrete with particles irradiated at 250 and 300 kGy, because the deformation values have minimal difference among them, which means to have certain control over the deformation, independently of the size and concentration of the tire particles. Thus, high irradiation doses produce physicochemical changes on the tire particles, mainly cross-linking of polymer chains, which allows high physical interactions with the concrete components.

II) Regarding to particle size, two behaviors are observed: a) For small size tire particles (0.85 mm), the deformation values gradually increase, b) an opposite behavior is observed for large particle size (2.8 mm). Following the dotted straight line, as reference for lower or higher values than that for control concrete; higher values are obtained for concrete with small size particles irradiated at 250 kGy and 300 kGy. Then, it is possible to have control on the concrete deformation by using high irradiation dose and small particles size; III) concerning to particulate concentration, the deformation decreases when the concentration increase, in consequence concrete is harder. The highest deformation values are obtained with 1 % of large size particles.

3.3. Elasticity modulus of concrete with non-irradiated and irradiated waste tire rubber particles

The elasticity modulus values of concrete cured at 28 days with non-irradiated and irradiated waste tire rubber particles are shown in Fig. 4. I) regarding to irradiation dose: a) concrete with non-irradiated particles had higher values respect to control concrete (named 0.97 GPa). The highest value was obtained for concrete with 1 % of small size particles, namely

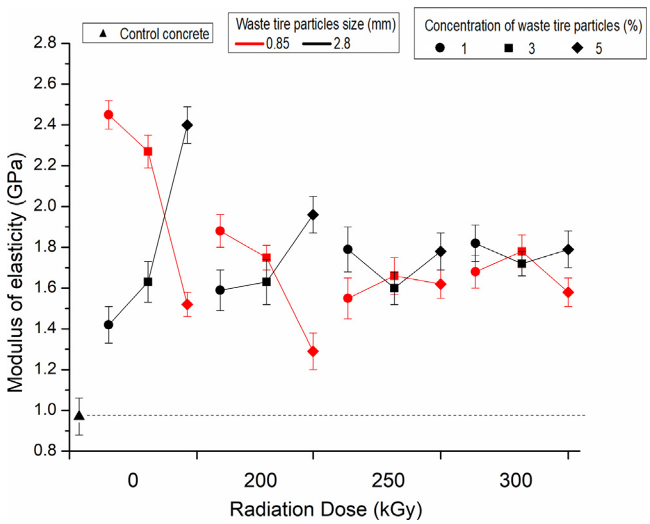

Fig. 4. Elasticity modulus of concrete with non-irradiated and irradiated waste tire rubber particles.

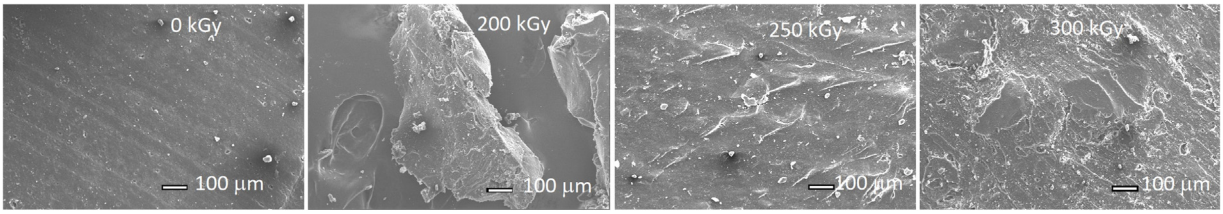

Fig. 5. SEM images of non-irradiated and irradiated waste tire rubber particles (amplification 100×).

2.45 GPa, which means an improvement of 161 % respect to control concrete. Similar improvement (147 %), is observed for concrete with 5 % of large size particles.

b) For concrete with irradiated waste tire particles, each elasticity value is higher than that for control concrete, but lower when comparing with those with non-irradiated particles. The highest values (1.96 GPa), were obtained for concrete with irradiated particles at 200 kGy, which means an improvement of 108 % respect to that for control concrete. The physicochemical changes produced by ionizing radiation on the tire particles are enough for modify the concrete elasticity. Small differences on the values are observed for concrete with irradiated particles at 250 kGy and 300 kGy, independently of the particle size. Thus, it is possible to have control on the elasticity modulus of concrete by using high radiation dose.

II) Respect to particle size, notable differences are observed: a) for concrete with non-irradiated particles, higher values are obtained with small size particles (0.85 mm); b) while for those with irradiated particles at 250 kGy and 300 kGy, the values had minimal difference, independently of the particle size; it was possible hold improvements around 108 %. Thus, when adding irradiated large size tire particles, is not necessary add more water, because the cross-linking of the polymer chains produced at high gamma dose, allows a hydrophobic surface on the tire rubber; III) Respect to the particulate concentration, two well-defined behaviors were observed: a) the values increase when particulate concentration increase, which was obtained for concrete with non-irradiated particles and concrete with irradiated particles at 200 kGy; b) the values decrease when particulate concentration increase, which was obtained for concrete with irradiated particles at 250 kGy and 300 kGy.

Thus, for to obtain a rigid concrete with non-irradiated particles, is necessary to add small size particles and low concentration of them, while for concrete with irradiated particles, is also necessary irradiate it at 200 kGy. Moreover, if the objective is to hold the hardness of concrete, independently of the particle size and concentration, is recommendable to irradiate at dose of 250 kGy and 300 kGy.

3.4. Morphological characterization of non-irradiated and irradiated waste tire particles

Scanning electron microscopy images of non-irradiated and irradiated waste tire rubber at an amplification of 100x are shown in Fig. 5. Non-irradiated particles show a smooth and grated surface with some small particles. For 200 kGy of radiation, the surface becomes rough with adhered particles. Roughness of the surface is most notable and larger cracks appear at 250 kGy of radiation. Finally, at 300 kGy, rougher surface, with more pronounced cracks and some small cavities are observed. These morphological changes, at 250 and 300 kGy, on the tire rubber particles allow to have control on the elasticity modulus of the concrete.

Due to importance of the morphological changes produced by irradiation on the tire rubber particles, in Fig. 6 amplificated SEM images at 1500x are shown. An homogeneous surface with scattered particles lower than 10 μm is observed for non-irradiated tire rubber. At 200 kGy is observed detachment of particles and increase of the roughness on the surface; but as dose increases to 250 kGy, more scrapped particles with larger sizes as well as oriented cracks are noticed. Finally at 300 kGy, well-defined cracks with a width size around 10 μm are obtained. Such results are consequence of the ionizing energy, which in a first stage produce free radicals and scission of polymer chains; but if irradiation dose increase, degradiation on the rubber surface is produced, manifest for the presence of detached particles, cavities and cracks.

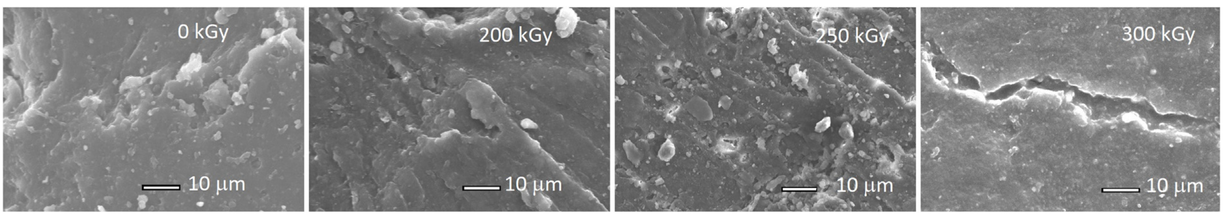

Fig. 6. SEM images of non-irradiated and irradiated waste tire rubber particles (amplification 1500×).

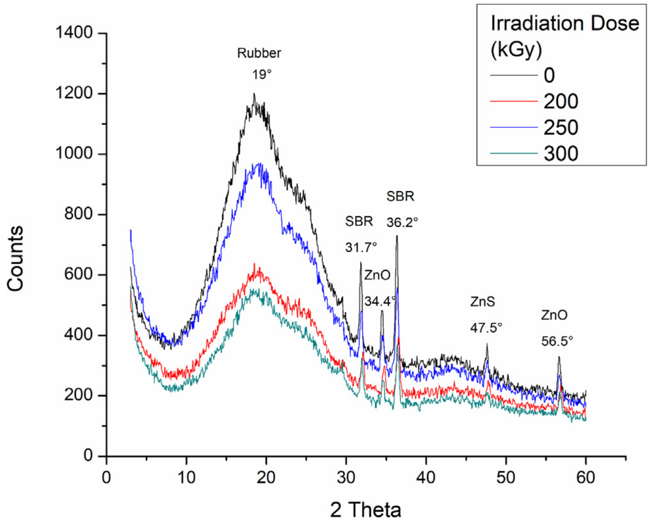

Fig. 7. XRD Spectra of non-irradiated and irradiated waste tire rubber particles.

3.5. Crystallinity of non-irradiated and irradiated waste tire rubber particles

Evaluation of the crystallinity of non-irradiated and irradiated waste tire rubber particles was made. The spectrum for non-irradiated tire particles show six crystalline peaks (Fig. 7). The most intense is located at $2\theta = 19^{\circ}$ which corresponds to natural rubber (NR) [26], acrylonitrile butadiene rubber (NBR) [27] and styrene butadiene styrene (SBS) [28]. Two less intense peaks located at $2\theta = 31.7^{\circ}$ and 36.2° correspond to styrene-butadiene rubber (SBR). Peaks at $2\theta = 34.4^{\circ}$ and 56.5° correspond to zinc oxide (ZnO), and peak at $2\theta = 47.5^{\circ}$ to zinc sulphide (ZnS); which are compounds widely used in rubber industry as activators on the sulphur vulcanization [29,30].

The crystalline arrangement is maintained in the tire rubber particles after irradiation, because the peaks are located in the same position ($2\theta^{\circ}$) than those for non-irradiated ones, but with lower intensities. Thus, the degree of crystallinity decreases according to irradiation dose increase. Thus, the lowest crystallinity is obtained at 300 kGy [26]. Moreover, the highest intensity values obtained at 250 kGy, can be related with the maximum cross-linking of the polymer chains produced by gamma rays.

3.6. FT-IR spectroscopy of non-irradiated and irradiated waste tire rubber particles

The FT-IR spectra of non-irradiated and irradiated waste tire rubber particles in the range of 4000–2000 cm^{-1} are shown in Fig. 8. The bands at 2913 and 2839 cm^{-1} correspond to stretching vibration of methylene group ($-CH_2-$) of the SBS, SBR

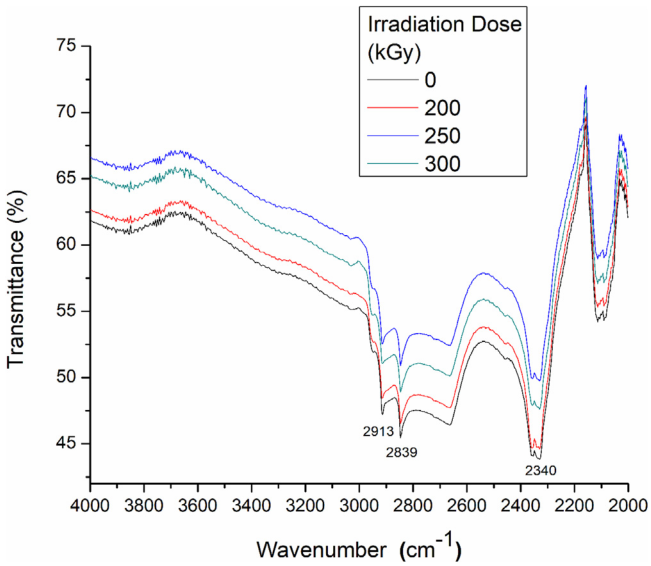

Fig. 8. FT-IR spectra in the (4000–2000 cm^{-1}) range for non-irradiated and irradiated waste tire rubber particles.

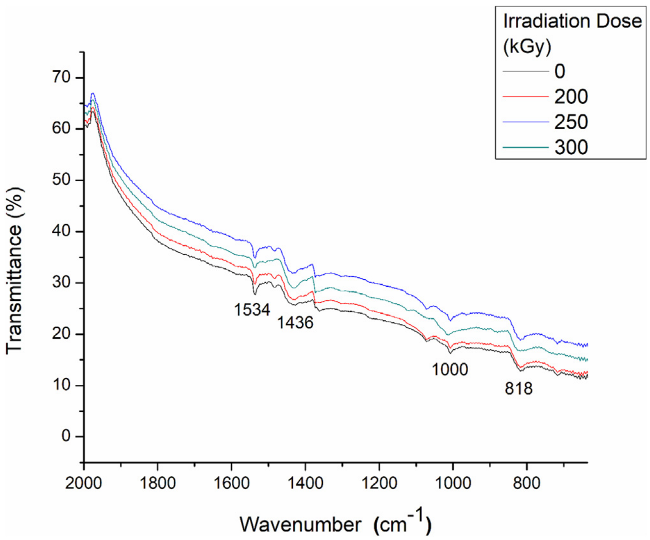

Fig. 9. FT-IR spectra in the (2000–735 cm^{-1}) range for non-irradiated and irradiated waste tire rubber particles.

and isoprene. While, the band at 2340 cm^{-1} correspond to nitrile group of the NBR. According to irradiation dose, the transmittance percentage increase for irradiated particles. The highest percentage is obtained for particles irradiated at 250 kGy.

FT-IR spectra in the range of 2000−735 cm^{-1} are shown in Fig. 9. The band at 1534 cm^{-1} corresponds to stretching vibration of C=C aromatic ring of SBS. While, the band at 1436 cm^{-1} corresponds to flexion vibration of methylene group ($-CH_2-$). There is a band near to 1000 cm^{-1} corresponding to bending vibration out-of-plane of C = C–H (trans-vinylene group) of NBR [31]. Finally, the band at 818 cm^{-1} corresponds to the stretching vibration of C–H. Respect to the irradiation dose, the transmittance percentage increase for irradiated particles. The highest percentage was obtained at 250 kGy, which is related with the maximum cross-linking of the polymer chains produced by gamma rays.

3.7. Raman spectroscopy of non-irradiated and irradiated waste tire rubber particles

The Raman spectra of non-irradiated and irradiated waste tire rubber particles are shown in Fig. 10. The highest intensities and luminescence of the Raman signals are obtained for non-irradiated and irradiated particles at 300 kGy. While, lower intensities with well-defined bands are obtained at 200 and 250 kGy.

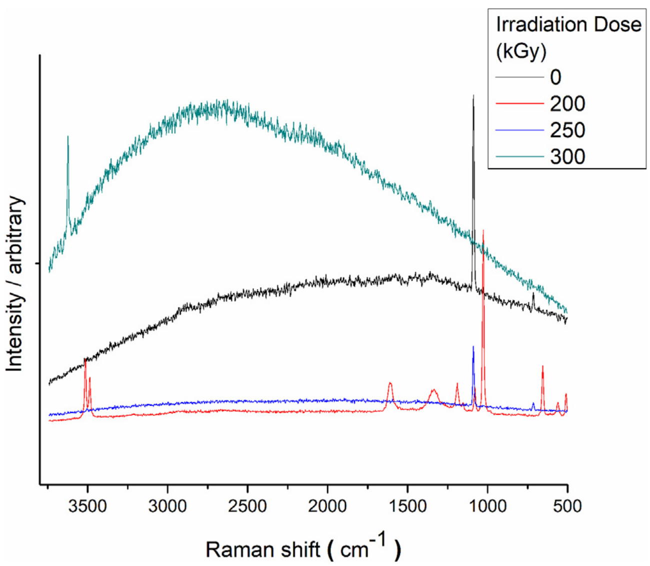

Fig. 10. Raman spectra of non-irradiated and irradiated waste tire rubber particles.

Table 4
Raman bands of non-irradiated and irradiated waste tire rubber particles.

Assignment	Wave number (cm^{-1})			
	0kGy	200kGy	250kGy	300kGy
ν Aromatic C-H	–	3511	–	3610
ν C=C Polybutadiene	–	1614	–	–
Aromatic plane	–	–	1101	–
ν_s Si-O-Si	1087	1087	–	–
Aromatic C–H in the plane	–	1015	–	–

Detected Raman bands of non-irradiated and irradiated waste tire rubber particles are shown in the Table 4. Non-irradiated tire particles show a signal at 1087 cm^{-1} corresponding to symmetric stretching vibration of Si-O-Si. Such chemical elements are present during rubber vulcanization process.

Well-defined signals at 200 kGy and 250 kGy are observed, which have lower intensities than those for non-irradiated particles. For 200 kGy, the bands: at 3511 cm^{-1} corresponds to stretching vibration of aromatic C–H; at 1614 cm^{-1} to stretching vibration of C=C, at 1015 cm^{-1} to the deformation in the plane of aromatic C–H; and at 1087 cm^{-1}. The intensities of these bands decrease for irradiated particles at 250 kGy, where is observed a band at 1101 cm^{-1} corresponding to the deformation in plane of aromatic styrene. Finally, particles irradiated at 300 kGy, show a band at 3610 cm^{-1} corresponding to stretching vibration of aromatic C–H.

3.8. UV–vis spectroscopy of non-irradiated and irradiated waste tire rubber particles

UV–vis spectra of non-irradiated and irradiated waste tire rubber particles are shown in Fig. 11. Signals lower than 300 nm correspond to electronic transitions $\pi\rightarrow\pi^*$; the band for butadiene is detected at 217 nm. The wavelength associated with the band gap of non-irradiated particles is 327 nm (3.79 eV). Very small shifts are observed for irradiated particles: 328 nm (3.78 eV), 333 nm (3.72 eV), and 329 nm (3.77 eV), for irradiation dose of 200, 250 and 300 kGy, respectively. Such values are typical of an insulating material, with covalent bonds and without delocalization of valence electrons in the hydrocarbon chains. Moreover, percentage of reflectance increase according to irradiation dose increase, with a minimal difference for 200 and 250 kGy, respect to that for non-irradiated particles. Nevertheless, at 300 kGy, higher difference on the percentage of reflectance is observed.

3.9. Thermal gravimetric analysis (TGA) of non-irradiated and irradiated waste tire rubber particles

Fig. 12 shows the TGA curves of non-irradiated and irradiated waste tire rubber particles. As can be seen the onset of degradation T0.1 (10 % of mass loss), the temperature for non-irradiated particles was located at 368 °C, which decrease 10 °C for particles irradiated at 200 kGy, and 5 °C for those irradiated at 250 kGy. Nevertheless, for higher irradiation dose, 300 kGy,

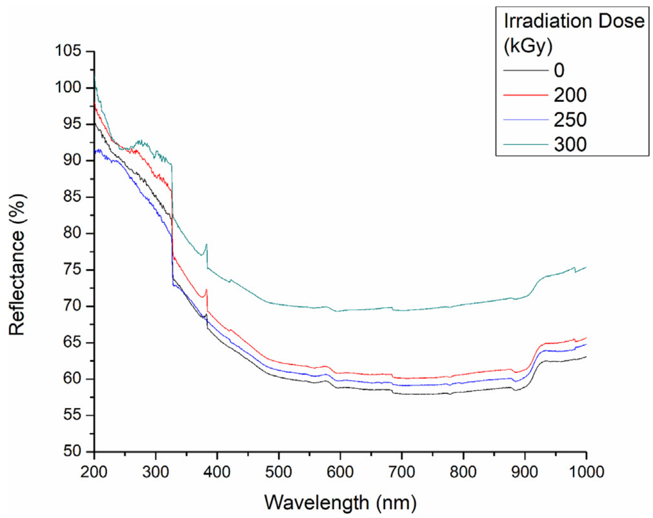

Fig. 11. UV–vis spectra of non-irradiated and irradiated waste tire rubber particles.

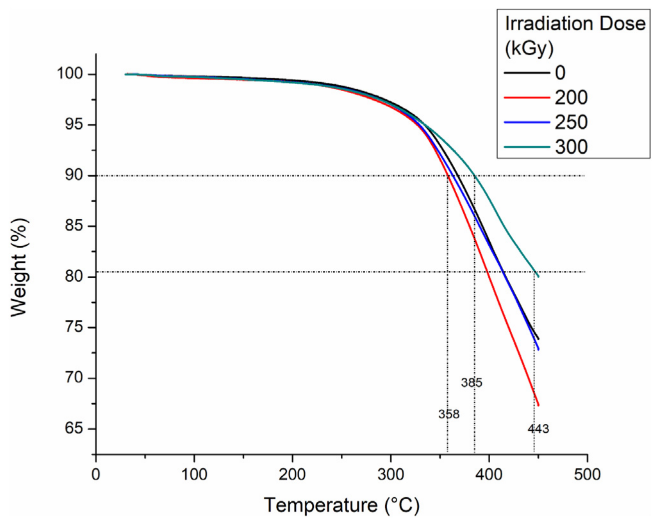

Fig. 12. TGA curves of irradiated and non-irradiated waste tire rubber particles.

an increment of 17 °C was obtained. Such increment on the temperature is related with cross-linking of polymer chains produced by gamma rays. As it is known, cross-linked structures need higher heat for their disintegration, while diminution on the temperature is related with scission of polymer chains.

Notable difference is observed for the onset of degradation T0.2 (20 % of mass loss). For non-irradiated particles, the temperature is located at 416 °C, which is the same for particles irradiated at 250 kGy. However, the temperature diminishes 17 °C for particles irradiated at 200 kGy, but it increases 34 °C for particles irradiated at 300 kGy. Thus, high ionizing radiation dose generate harder tire rubber, then more heat flux is necessary for the transition from amorphous to soft state, where covalent and van der Waals bonds begin to weaken, arising local movements of polymer chain segments.

3.10. Differential scanning calorimetry (DSC) of non-irradiated and irradiated waste tire rubber particles

In accordance with the DSC thermograms shown in Fig. 13, the heat flow for non-irradiated waste tire particles diminishes gradually around 300 °C. An exothermic peak is obtained at 373 °C with a heat flow of 19.4 mW. The heat release is associated with an exothermic reaction. Similar behavior is observed for irradiated particles at 200 kGy, but the heat flow is 16.9 mW, which is 12 % lower than that for non-irradiated particles. Minimal difference on the heat flow exist for particles irradiated at 250 kGy and non-irradiated ones. However, for tire particles irradiated at 300 kGy, the exothermic peak is not

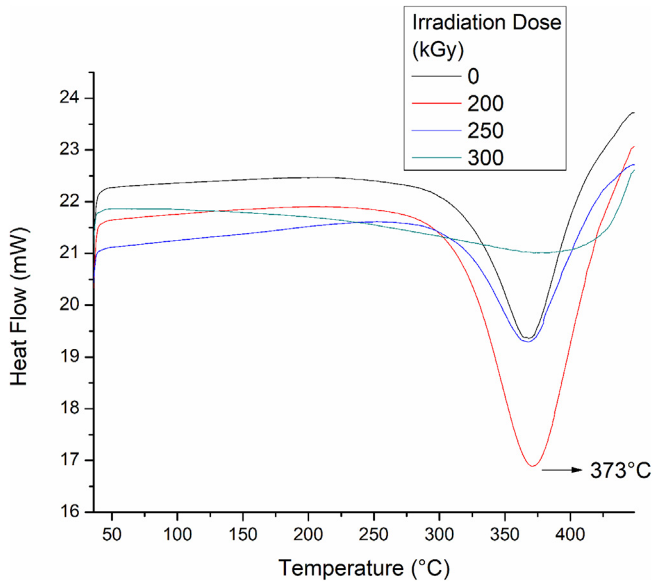

Fig. 13. DSC curves of non-irradiated and irradiated waste tire rubber particles.

obtained, whereby, tire rubber becomes more amorphous, due to cross-linking of polymer chains, which disrupt the crystalline phase.

4. Conclusions

The effects of gamma rays and waste tire rubber particles were studied in concrete produced with cement, silica sand, rock crushed and water. The results were analyzed in terms of the experimental parameters: gamma irradiation dose (200, 250 and 300 kGy), and size (0.85 and 2.8 mm) and concentration (1, 3 and 5 wt. %) of waste tire rubber particles.

Improvements on the mechanical properties of concrete depend mainly of the irradiation dose, followed by the particles size, and to a lesser extent of tire rubber concentrations. Respect to irradiation dose, improvement up to 108 % on the elasticity modulus, and up to 13 % on the deformation were obtained. In the case of particles size, concrete with large size particles had the highest elasticity modulus and deformation values. According to the particulate concentration, the highest mechanical values were obtained when adding 1 % of tire rubber particles. In summary, highest elasticity modulus values are obtained with the combination of high concentration and large size of waste tire rubber particles. Moreover, it is possible to have control on the concrete deformation when using irradiated particles.

Improvements on the elasticity modulus of the concrete can be related with the physicochemical changes produced by gamma radiation on the waste tire particles. The elasticity modulus is favored when surface of tire rubber becomes rougher with large cracks and some small cavities. Such morphologies are due to the cross-linking of polymer chains, which were corroborated by thermal analysis, is to say, high irradiation dose produce a harder tire rubber, then more heat flux is necessary for the transition from amorphous to soft state. Finally, chemical structure of the tire rubber does not change, because irradiated particles have the same infrared bands but different intensities. Similar effects were obtained for the transmittance and reflectance percentages on the UV–vis spectra. However, a more detailed study is required for Raman spectra of the tire rubber irradiated at 300 kGy, where no defined peaks were observed.

Declaration of Competing Interest

The authors do not have a direct financial relation or conflict of interests with the commercial identities mentioned in this paper, and the commercial trademarks only were reported to guarantee the reproducibility, in the same conditions, of the different tests.

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