# Current microscopy contributions to advances in science and technology

FORMATEX
Microscopy Series Nº 5

VOL. 2

**Edited by**

A. Méndez-Vilas

ISBN-13 Vol. 2: 978-84-939843-6-6
ISBN-13 Collection: 978-84-939843-4-2

Formatex Research Center
C/ Zurbarán 1, 2º - Oficina 1
06002 Badajoz
Spain
http://www.formatex.org

Printed in Spain

# TABLE OF CONTENTS

## VOL. 1

## VOL. 2



## Advances in Instrumentation and Techniques

## Educational materials on Microscopy



## Applications in Physical/Chemical Sciences

# Electron Microscopy for the evaluation of concrete surfaces modified by gamma radiation

**L.I. Avila-Córdoba**[1], **G. Martínez-Barrera**[2], **F. Ureña-Nuñez**[3] and **C.E. Barrera-Díaz**[1]

[1]Centro Conjunto de Investigación en Química Sustentable (CCIQS), Universidad Autónoma del Estado de México – Universidad Nacional Autónoma de México (UAEM-UNAM), Carretera Toluca-Atlacomulco, km 14.5, Unidad El Rosedal, C.P. 50200, Toluca México.
[2]Laboratorio de Investigación y Desarrollo de Materiales Avanzados (LIDMA), Facultad de Química, Universidad Autónoma del Estado de México, Km.12 de la carretera Toluca-Atlacomulco, San Cayetano 50200, México.
[3]Instituto Nacional de Investigaciones Nucleares, Carretera México-Toluca S/N, La Marquesa Ocoyoacac 52750, México.

As we know the electron microscopy has shown its effectiveness as tool for surfaces analysis. Depending on the material is possible to describe surface features as roughness, smoothness, and so. In the case of composite materials is essential the analysis of the contributions of each component of the composite. For the case of concrete or mortar materials, some approaches have been developed and general statements are taken as standard parameters. The hydraulic concrete derived from a mixture of cement, rough and fine aggregates and water. Each one contributes on the final features of concrete, including the mechanical properties. The morphology of each component takes into account size, shape, roughness, etc. In this chapter we discuss the importance of the electron microscopy for to describe the influence of the components after mechanical testing, and some predictions can be planned for to avoid fractures.

**Keywords:** scanning electron microscopy; hydraulic concrete; polymer concrete; gamma radiation.

## 1. Introduction

Ordinary Portland Cement Concrete (PCC) is one of the oldest man-made materials and is important among inorganic building materials. The success of PCC as a building material derives mainly from its inexpensive cost and many desirable properties. The use of Portland cement, however, is not limited to construction of buildings but may also be used, as an example, for waste immobilization. The components of PCC are well known: rocks and/or gravel (coarse aggregate), sand (fine aggregate), hydrated Portland cement, and usually voids – with the coarse aggregate making up the majority of the concrete and the hydrated Portland cement binding the whole material.

Development of another alternative to PCC was begun in the 1960s with the incorporation of organic polymers into cement concrete, giving a new class of composite building materials. Since that time, knowledge of so-called Polymer Concrete (PC) has significantly progressed. Polymer concrete is a composite material formed by combining mineral aggregates (such as sand or gravel) with a monomer, usually of a thermoset polymer resin. To form the final concrete product, the monomer must be cured, forming a network of polymer chains from the original monomeric compound. Therefore in PC we have a polymeric matrix as the continuous phase and dispersed inorganic particles as a discrete phase [1].

Typically PC has a longer maintenance-free service life than PCC and possesses also other advantages compared to PCC such as: increased bond strength (bonding to previously existing concrete); increased freeze-thaw resistance; high abrasion resistance; increased flexural, compressive and tensile strengths; fast setting times (curing within 1 or 2 h); good durability; improved chemical resistance in harsh environments [2, 3]. Moreover, they exhibit good creep resistance [4], and are highly UV resistant due to the very low polymer content and inert fillers. On the other hand, they exhibit reduced elastic modulus. The loss of strength can be attributed to an increase of porosity in PCs with increased capillary diffusion of solutions, which weakens the bond between the aggregate and the matrix [5].

## 2. Portland Cement Concrete after gamma irradiation

In the case of hydraulic concrete (PCC), some modifications on the cement and silica sand have been done by using gamma radiation; such materials are mixing into the concrete. In other case all concrete components are mixed and then the concrete specimens are irradiated. Both kinds of concretes are evaluated by mechanical tests. The results are different, and the scanning electron microscopy has been a good tool for to evaluate the contribution of each component in non-irradiated and irradiated concretes.

For the morphological characterization, after mechanical testing, some fractured hydraulic concrete pieces were dried qin a rotovapor for 24 hours. After, they are vacuum-coated with carbon (coating thickness between 3 to 10 nm) in a vacuum pump at 50 mTorr. Then the surfaces of fractured zones are analyzed by scanning electron microscopy (SEM) in the secondary electron mode, which provides good images of distribution of dispersed phases in a matrix [6 - 10].

Moreover, the surfaces of silica sand and marble, before and after irradiation were analyzed following the specifications as fracture concrete samples. The secondary electron mode is preferred in the present case, because provided good contrast between the constituents. While for instance in characterization of polymer + metal hybrids micro powder, backscattered electrons provide a better contrast [7, 11].

Surface modifications of silica sand are shown in Figure 1. Evident is deterioration of silica sand surfaces with increasing irradiation. For non-irradiated silica sand a homogeneous surface is seen, with a few cracks ≈ 5 μm long (Figure 1a); when increasing the radiation dose, several particles smaller than 5μm in average size appear (Figure 1b); and finally for the high dose of 150 kGy deteriorated surface with several cracks (Figure 1c) is seen. The mechanical performance of the concrete can be related to morphological changes on the surfaces. Moreover, some conclusions can be done after analyzing surfaces of the concrete components after submitted to gamma radiation. For example, the cracks propagating on surfaces of silica sand particles can relate with the lower compressive strength values obtained at higher gamma dosages.

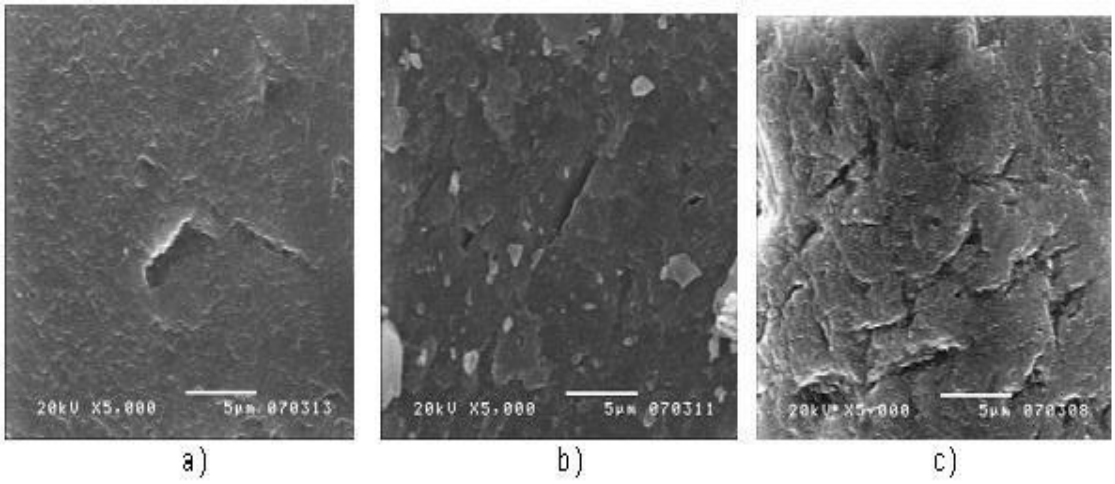



**Fig. 1** SEM images of silica sand: a) non-irradiated, b) irradiated at 50 kGy, and c) irradiated at 150 kGy.

A literature survey shows that relatively little attention has been paid to the morphology of silica sand and its contribution to mechanical improvement of concrete. Evident in Figure 2 are morphological changes dependent on the irradiation dose. Crazes and some grooves are observed. The number of the crazes increases with the irradiation dose; the crazes are well developed at 150 kGy, about 100 μm long and a certain "branching" tendency is seen. The wrinkles have more contact points – thus providing stronger adherence of sand to the hydrated cement. Herein lay an explanation of the property improvement resulting from irradiation [8].

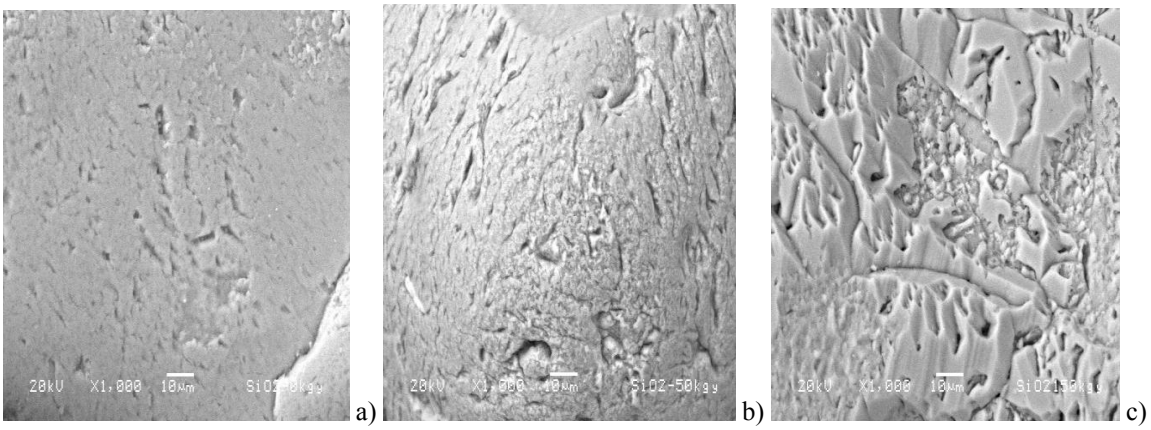



**Fig. 2** SEM images of silica sand: a) non-irradiated, b) irradiated at 50 kGy, and c) irradiated at 150 kGy.

We see in Figure 3 that the marble morphology exhibits similar behavior to the silica sand. That is, for non-irradiated marble, several particles are seen (Figure 3a); after increasing the gamma radiation dose to 50 kGy, more particles with larger sizes appear (Figure 3b). For the high dose of 150 kGy, the particle size is still larger due to degradation of the marble (Figure 3c). As noted previously, mechanical performance of the concrete can be related to morphological changes on the surfaces. In some cases the dynamic elasticity modulus $E_d$ values of concretes are lower than those for non-irradiated, thus a more ductile concrete is formed - pertinent in the case of seismic events [9].

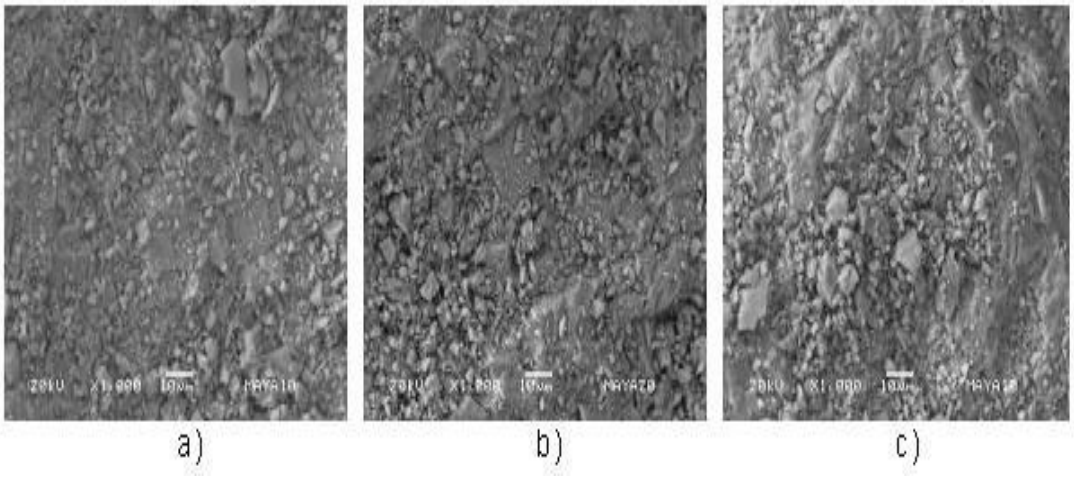



**Fig. 3** SEM images of marble: a) non-irradiated, b) irradiated at 50 kGy, and c) irradiated at 150 kGy.

Concretes consisting of Portland cement, silica sand, marble and sludge were developed. The sludge was subjected to two series of treatments. In one series, coagulants were used, and in the other series, an electrochemical treatment was applied with several starting values of pH. The compressive strength, compressive strain at yield point, and static and dynamic elastic moduli were determined [12]. The sludge generated by the electrochemical process at pH = 7 and the fractured concrete specimens were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDS). The sludge shows a heterogeneous morphology, as shown in Fig. 4a. Its elemental composition as determined by EDS includes carbon (20.9 %), oxygen (46.9%), iron (16.2%), and sodium (2.2%) as the main elements (Fig. 4b).

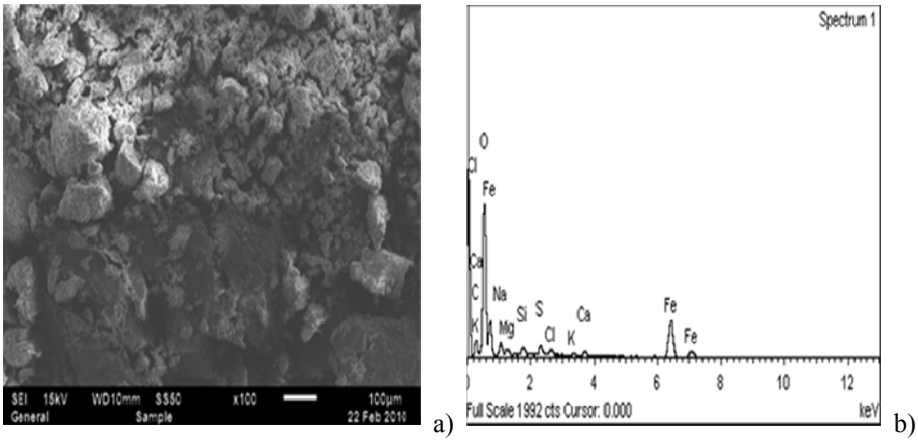



**Fig. 4** a) SEM image of dry sludge, and b) Microanalysis image (EDS) of dry sludge.

Figure 5 shows the morphology of the fractured surfaces of the concretes (seven days curing) subject to compressive testing. For the concrete with higher silica sand content, the surface of the sludge containing material (Fig. 5b) is less rough than the specimen without sludge (Fig. 5a). The sludge seems to acts as a wrapper for the marble particles. For the concrete with lower silica sand content, both surfaces are fairly similar (Figs. 5c and 5d). Somewhat larger marble particles are seen in the absence of sludge. From Figure 5d, it is inferred that the amount of sludge is insufficient to cover all silica sand particles. The presence of sludge has beneficial effects on the long term properties and for to improve the compressive strain at yield point of concrete.

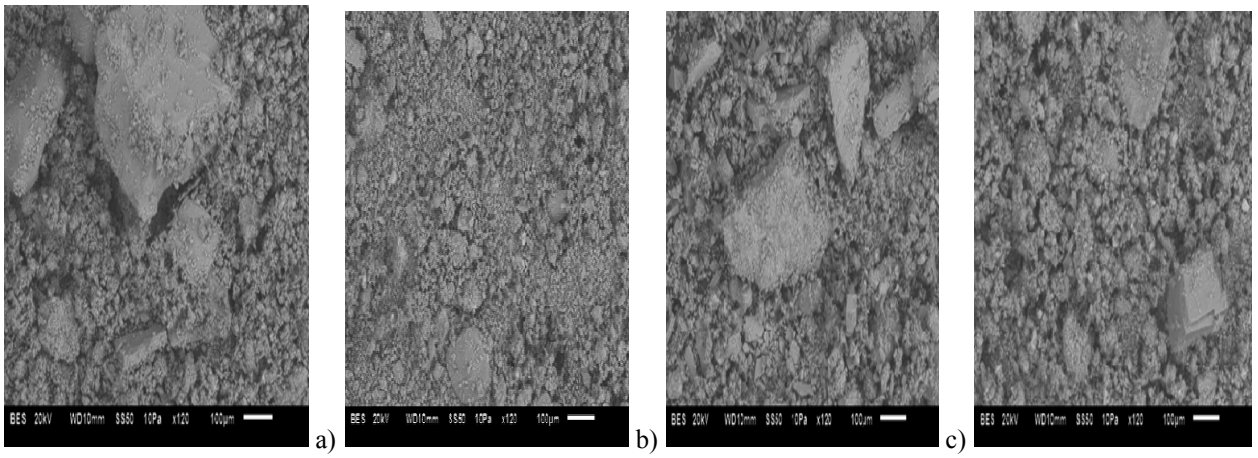


**Fig. 5** SEM images of the curing concrete (at 7 days) after compressive testing: a) Higher silica content, b) Higher silica content and sludge, c) Lower silica content, and d) Lower silica content and sludge.

## 3. Polymer Concrete after gamma irradiation

As we remind, polymer concrete is a composite material formed by combining mineral aggregates (such as sand, marble, CaCO3 or gravel) with a monomer, usually of a thermoset polymer resin. To understand the changes of the elasticity modulus of the polymer concrete, the neat polyester resin is irradiated and studied the morphological changes by SEM (Figure 6). For non-irradiated resin, a homogeneous surface is seen. It contains regions not fully polymerized by the MEKP catalyst (Figure 6a). When applying 50 kGy of irradiation (Figure 6b), a surface consists of several constraining regions, apparently responsible for the elasticity modulus. At 100 kGy, the gamma radiation results in the presence of two morphologies on the resin surface, constrained regions, and voids, what leads to the highest elasticity modulus (Figure 6c).

Improvement in mechanical properties caused by irradiation is clearly related to morphology of the components and the void volume in the composites. The larger the irradiation dose, the larger are the void volumes, caused by morphology deteriorations suffered by the polyester resin. An adequate aggregate gradation can provide low void volumes and thus good mechanical strength. Variations in the gamma radiation dose enable modification of the void volume and thus higher compressive strain [11].

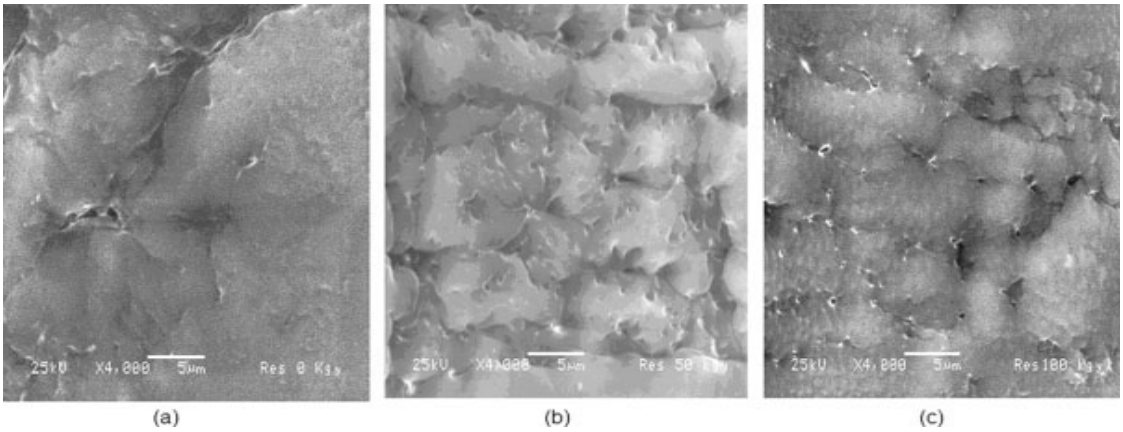



**Fig. 6** SEM images of polyester resin: a) non-irradiated, b) irradiated at 50 kGy, c) irradiated a 100 kGy.

The high compressive strain values can be explained in terms of surface morphology of the polymer concrete. For irradiated polymer concrete at 5 kGy, a heterogeneous morphology is observed, including the aggregate particles covered by polyester resin (Figure 7a). When increasing the applied radiation dose, a softer surface is seen and the aggregate particles are fully covered (Figure 7b). This situation is a consequence of crosslinking of the chains in the polyester resin. Moreover, for higher applied doses, the polyester resin is constrained, the surfaces show more agglomeration regions, what produces the highest compressive strain values (Figure 7c). In the 0–50 kGy interval, there is chain reorientation due to the polymerization in the polyester resin with an increase in the crystallinity; however, if the radiation process goes on, the damage can be permanent. The lowest compressive strain value is at 10 kGy, what implies there is an influence of the polyester resin.

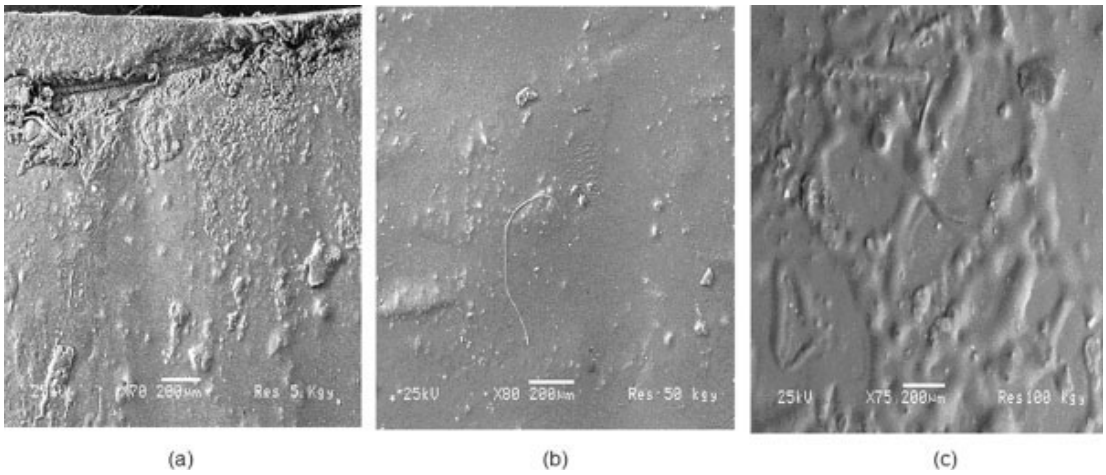



**Fig. 7** SEM images of polymer concrete irradiated at: a) 5 kGy, b) 50 kGy, and c) 100 kGy.

The compressive strain values can be related to the morphology of the polymer concrete surfaces fractured after testing. For polymer concrete irradiated at several doses and elaborate with two different sizes of the marble particles. The compressive strain values for 5 and 10 kGy are the same, but lower by 29% at 50 kGy. At low doses the marble particles are covered by the polyester resin; several scrap particles (produced by the compression force) smaller than 10 μm are seen (Figures 8a and 8b). When increasing the applied radiation dose, a larger number of scrap particles and cracks passing through the marble particles are seen (Figure 8c). A large number of such cracks provide more ductile concrete. The cracks are a consequence of the polyester constraints resulting from crosslinking of the chains in the polyester resin.

The compressive strain behavior of polymer concretes with three-particle sizes, has three stages: a) a decrease from non-irradiated to 10 kGy; b) an increase up to 50 kGy; and c) a decrease at higher doses (100 and 150 kGy). Thus, the combination of three different particle sizes results in a harder material. Compressive strain values are lower than those for polymer concretes with two particles sizes. Then combination of two or three different particle sizes into the concrete generate a harder material - instead of a ductile material created when only one particle size is used [10].

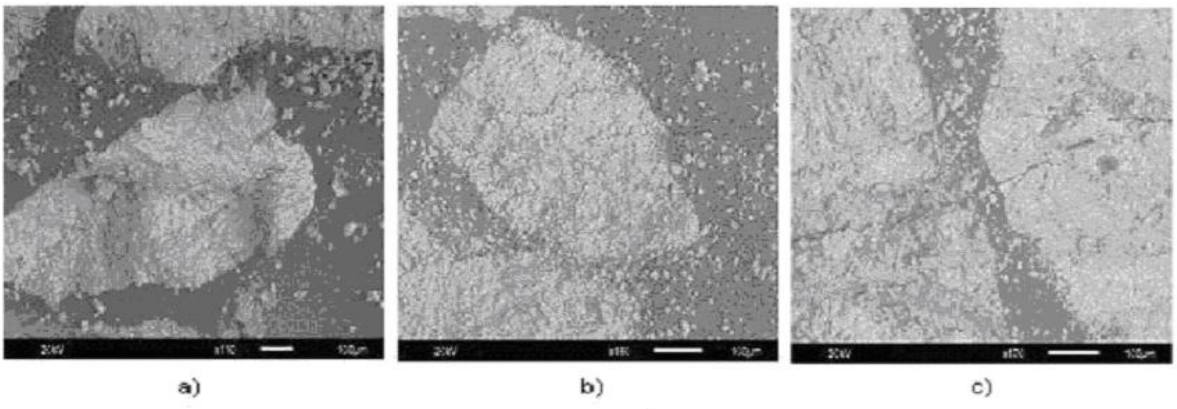



**Fig. 8** SEM images of polymer concrete irradiated at: a) 5 kGy, b) 10 kGy, and c) 50 kGy.

The morphological modifications of marble after irradiation are related with mechanical properties of the concrete. Homogeneous surfaces on marble particles are seen for non-irradiated samples (Figure 9a). When increasing the dose to 100 kGy, scraped particles are generated (Figure 9b), and for a dose of 150 kGy a partial destruction of the marble particles (Figure 9c). Gradual deteriorate on the marble particles when increasing the applied dose, and thus gradual lowering of the compressive strength [13].

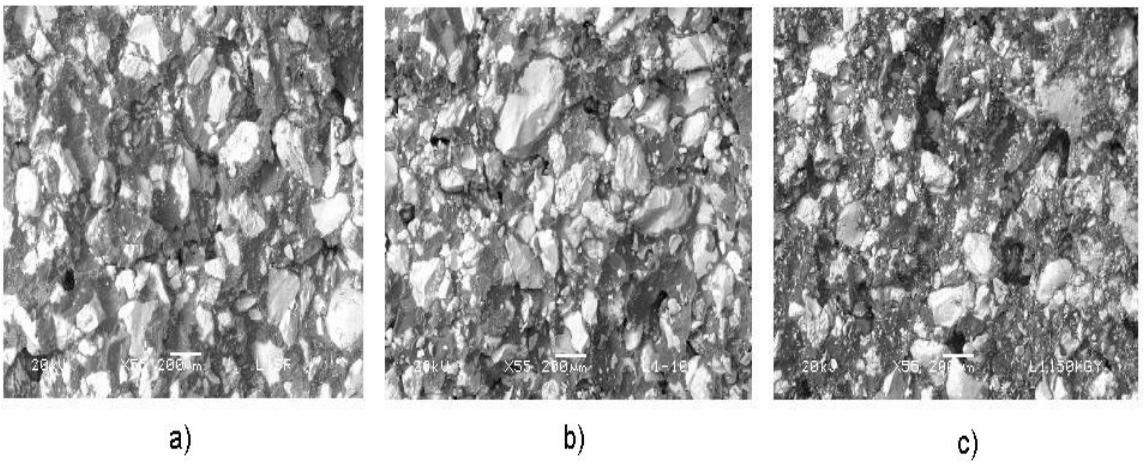



**Fig. 9** SEM images of fractured zones of concretes: a) non-irradiated, b) irradiated at 100 kGy, and c) irradiated at 150 kGy.

In Fig. 10 we show the fracture zone after testing the polymer concrete with 38% of resin and 62% of silica sand. For non-irradiated PC an analysis of silica sand and polyester resin was carried out (Fig. 10a). First, sand particles are well visible with sizes below 50 mm, contributing to the material resistance against deformation under a compressive load. Then, the particles tend to disintegrate; the original particles had the diameters of 150 mm on the average. The resin has a homogeneous surface and totally covers the sand particles [7].

When increasing the irradiation dose, the mechanical features are improved. However, for the high level radiation, namely 100 kGy, the mechanical parameters decrease. In the SEM image corresponding to 100 kGy (Fig. 10b), we observe less disaggregate sand particles whose sizes are not smaller than non-irradiated PC. Moreover, crack formation in the resin is seen, thus, a separation between the sand particles and the resin occurs. This causes lowering of both the compressive strength and strain values. On the other hand, we get high elastic modulus. At the highest radiation dose of 150 kGy, an evident separation between resin and the particles is seen. Some small particles, with the diameter below 50 mm on the average, are observed (Fig. 10c). In principle, when the PC has more space between resin and the particles (caused by gamma radiation), the elastic modulus increases but the compressive strength decreases.

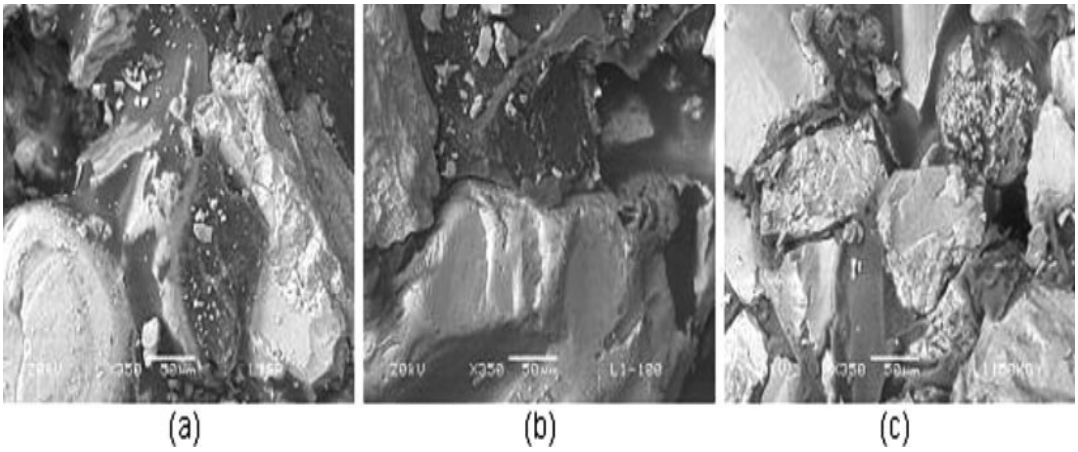
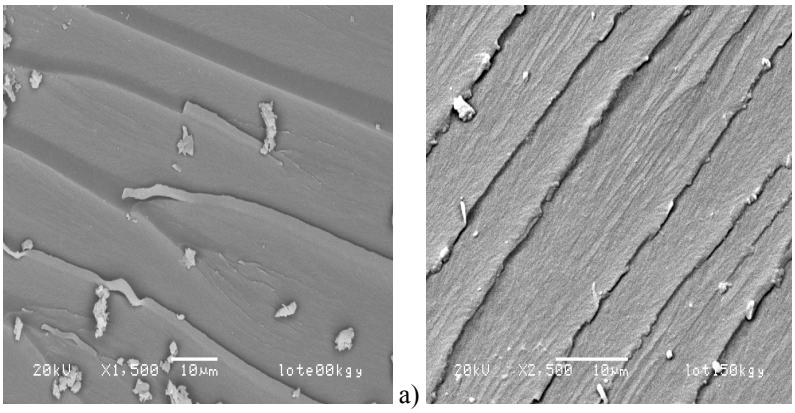



**Fig. 10** SEM images of polymer concrete after compressive test: a) non-irradiated, (b) irradiated at 100 kGy, and c) irradiated at 150 kGy.

Moreover, the morphology of the non-irradiated resin shows a homogeneous surface (Figure 11a). For higher doses striations are seen, apparently a consequence of the resin contraction (Figure 11b). We emphasize that the resin provides major contributions to the mechanical improvement of the concrete. Then, if a sand particle is present in a non-irradiated resin matrix, it will be surrounded by the resin. When the radiation has been applied, the resin will start its polymerization, what will cause the following effects: breakdown of the resin (cracks) and resin contraction with pulling out from the sand particles. As already reported by Ismail et al., the interaction between cement constituents and polyester formed in the pores under the effect of gamma irradiation contribute to an improvement in the mechanical strength [14].

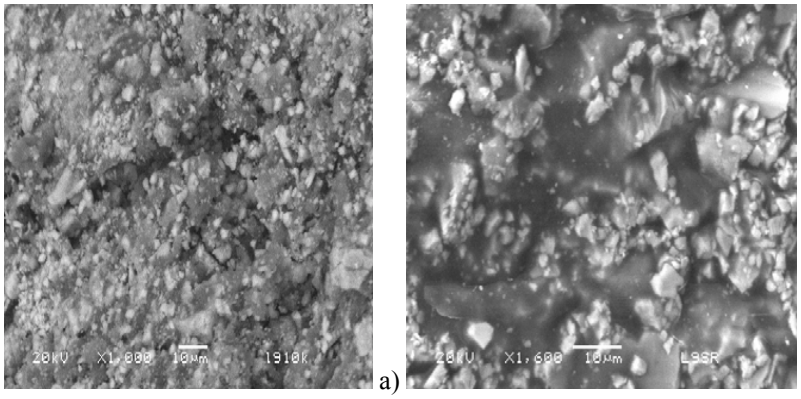
 




a) b)

**Fig. 11** SEM images of the polyester resin: a) non-irradiated, b) irradiated at 150 kGy.

The surfaces of the fractured zone of the manufactured polymer concrete, before and after irradiation, were analyzed by scanning electron microscopy. The concretes were elaborated with insaturated polyester resin and $CaCO_3$ particles. For the concrete irradiated at 10 kGy, when adding more solid $CaCO_3$ particles (Figure 12a), strong interactions appear, resulting in a hard material. As a consequence, significant restrictions on molecular mobility of the polyester resin around the $CaCO_3$ particles occur and an increment of the stiffness results. This does not happen when the samples contain less $CaCO_3$ particles (Figure 12b), weak interfacial interactions are present and the elastic modulus diminishes.




a) b)

**Fig. 12** SEM images of irradiated polymer concrete at 10 kGy, with: a) 46 % of the resin, b) 60 % of the resin.

It was suggested by the Zagreb group that the degree of the reinforcement of the composites may be a result of interdiffusion and entanglements between the homopolymer and polymer molecules grafted on the CaCO3 surface and the polymer matrix molecules [15].

For samples irradiated up to 10 kGy both compressive strain and compressive modulus of elasticity increase; we can presume that the polymerization of the resin still is not complete; more polymerization can be achieved by the irradiation energy input as discussed by Saiter and collaborators [16]. The Rouen group points out that two post-curing processes are necessary. With these treatments it is possible to get ≈ 95 % of total polymerization. In our case, by means of applied radiation it is possible to obtain lower compressive strain but an increase of the compressive modulus of elasticity. Moreover, the effects of the radiation up to 10 kGy allow formulating the following rule: higher concentrations of the resins results in higher values of the compressive modulus of elasticity.

According to the electron microscopy analysis, changes in the mechanical properties are related to the distribution of the $CaCO_3$ particles in the polyester resin and the adhesion between them. We emphasize that the resin provides major contributions to the mechanical improvement of the concrete. Differences in mechanical properties are significant when comparing to the non-irradiated resin: 223% for compressive strength, 66% for the compressive strain, and 105% for the compressive modulus of elasticity.

**Acknowledgements.** Mr. Miguel Martínez López and Ms. Elisa Martínez Cruz graduated students at the Materials Science Program (UAEM) have participated in the experiments. CONACYT grant 153828.

## References

[1] Martínez-Barrera G, Vigueras-Santiago E, Gencel O, Hagg Lobland HE. Polymer concretes: a description and methods for modification and improvement, *J. Mater. Ed.* 2011; 33: 37-52.
[2] Fowler DW. Polymers in concrete: a vision for the 21st century, *Cement & Concrete Composites* 1999; 21: 449-452.
[3] Vipulanandan C, Paul E. Characterization of polyester polymer and polymer concrete, *Journal of Materials in Civil Engineering* 1993; 5: 62 - 82.
[4] Reis JML, A comparative assessment of polymer concrete strength after degradation cycles, in *Mechanics of Solids in Brazil 2009,* Brazilian Society of Mechanical Sciences and Engineering, Brazil; 2009.
[5] Ahn N. Effects of diacrylate monomers on the bond strength of polymer concrete to wet substrates *J. Appl. Polym. Sci.* 2003; 90: 991-100.
[6] Martínez-Barrera G, Espinosa-Pesqueira ME, Brostow W. Concrete + polyester + $CaCO_3$: Mechanics and morphology after gamma irradiation, *e-Polymers* 2007; 83: 1-12
[7] Martínez-Barrera G, Texcalpa-Villarruel U, Vigueras-Santiago E, Hernández-López S, Brostow W. Compressive strength of Gamma-irradiated polymer concrete, *Polym. Compos.* 2008; 29: 1210-1217.
[8] Martínez-Barrera G, Martínez-Hernández AL, Velasco-Santos C, Brostow W, Polymer concretes improved by fiber reinforcement and gamma irradiation, *e-Polymers* 2009; 103: 1-14.
[9] Martínez-Barrera G, Menchaca-Campos C, Vigueras-Santiago E, Brostow W. Post-irradiation effects on Nylon-fiber reinforced concretes, *e-Polymers* 2010; 42: 1-13.
[10] Martínez-Barrera G, Brostow W. Effect of marble particle size and gamma irradiation on mechanical properties of polymer concrete, *e-Polymers* 2010; 61: 1 – 14.
[11] Martínez-Barrera G, Giraldo LF, López BL, Brostow W. Effects of gamma radiation on fiber reinforced polymer concrete, *Polym. Compos.* 2008; 29: 1244-1251.
[12] Barrera-Díaz C, Martínez-Barrera G, Gencel O, Brostow W, Bernal-Martínez LA. Processed wastewater sludge for improvement of mechanical properties of concretes, *Journal of Hazardous Materials* 2011; 192: 108 – 115.
[13] Martínez-Barrera G, Ureña-Nuñez F, Gencel O, Brostow W. Mechanical properties of polypropylene-fiber reinforced concrete after gamma irradiation, *Composites: Part A* 2011; 42: 567 – 571.
[14] Ismail MR, Ali MA, EI-Milligy AA, Afifi MS. Physico-chemical studies of gamma-irradiated polyester - impregnated cement mortar composite, *J. Radioanal. Nucl. Chem.,* 1998; 238: 111-117.
[15] Leskovac M, Kovacevic V, Lucic Blagojevic S, Vrsaljko D, Volovsek V. Pre-treatment of $CaCO_3$ nanofiller by irradiation in the presence of vinyl monomers for the preparation of poly(vinyl acetate) composites, *e-Polymers* 2004; 33: 1-13
[16] Delahaye N, Marais S, Saiter JM, Metayer M. Characterization of unsaturated polyester resin cured with styrene, *J. Appl. Polym. Sci.* 1998; 67: 695-703.