



Concrete + polyester + CaCO₃: Mechanics and morphology after gamma irradiation

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Abstract: We have studied effects of gamma radiation on mechanical performance of polymer concrete (PC) containing varying concentrations of an unsaturated polyester resin and calcium carbonate. The compressive strength values increase from the zero dose (non-irradiated PC) to 10 kGy; afterwards we find a periodical change as a function of the resin concentration. The highest compressive strength corresponds to the highest resin concentration but the changes are not too large. Compressive strain values also go symbiotically with the resin concentration. All our composites - including irradiated and non-irradiated - have higher strength values than those reported for earlier polyester + concrete materials. The compressive modulus values follow the same pattern as the compressive strength and strain.

Introduction

Cement and concrete belong to one of the oldest materials used by mankind, with the Portland cement as the leader in terms of volume [1, 2]. The Portland cement concrete (PCC) is a mixture of cement, fine and coarse aggregates and water. The PCC is utilized most often due its wide range of applications (structures, blocks, pavements, etc). PCC has a number of advantages: high compressive strength, durability and plasticity. However, PCC is also characterized by low tensile strength, high permeability resulting in trapping water and high deterioration caused by acid attacks. Given this situation, various ways to improve concrete have been developed, including particle packing [3], cement immobilization [4], making macro-defect-free cements [5], or else by using polymeric materials.

Given the properties of concrete without polymer reinforcement, the desired effects of adding a polymer include achieving high compressive and flexural strength, high impact and abrasion resistance, service possible in adverse environments (wind, moisture, etc.), lower weight and lower costs. Along these lines, polymer concrete (PC) is a particulate composite in which a thermoset resin binds inorganic

aggregates. This is in contrast to PCC in which the binding is a result of interaction of cement with water, a process which takes years – although the main effects are seen within days. Thus, in a PC we have a polymeric matrix and dispersed particles for strengthening phases. Since curing of that matrix takes place in one or two hours from the start, we have an important advantage of PC over PCC. Fast curing should also provide a longer maintenance-free service.

Even in PPC structures in fact PC is used as a very good repair material for the damaged structure elements. For example, deterioration of PPC caused largely by trapping water inside the structure and by acid attacks can be remedied by using a polymer with a minimum of open voids combined with a hydrophobic nature and chemical inertness. Moreover, the extent of waterproof characteristics can be improved by controlling the amount of the polymer used - as a function of the accessibility of the pores to be filled and also of the impregnation time.

In principle, PCC deterioration can be at least slowed down by taking advantage of the PC constituents. Thus, thermoset polymers exhibit hydrophobic nature and chemical inertness - which restrains formation of voids. Commonly used thermosets are polyester resins with low prices and good corrosion properties. For example, orthophthalic pre-accelerated polyester resin has the flexural strength of 119 MPa [6]. Inorganic aggregates which bind to the resins as dispersed particles of strengthening phases are important. The most used are silica sand, gravel or fly ash; their individual roles depend on the particle size and the final application of the PC. We also have in PCs an initiator and a promoter - for initiating the free-radical polymerization process. Examples are methyl ethyl ketone peroxide (MEKP), amine or benzoyl peroxide (BZP) as initiators, and cobalt naphthenate or dimethyl-para-toluidine (DMPT) as promoters; the concentrations used depend on the resin content [6].

Fine and coarse aggregates in PCs include river sands and gravels or crushed sands. Rocks are recommended for PCC. Low moisture content, cleanness, and good quality are usually required for aggregates in the preparation of PC. Thus, aggregates sometimes need to be oven-dried before mixing.

Depending on the application, different characteristics are found for fine aggregates, for example: a) particle sizes from 0.84 to 0.59 mm (20-28 mesh) used in fracture studies, b) sand used in the foundry industry (20-28 mesh) for the compressive and fracture behavior determination [6]. In this work we have used calcium carbonate (CaCO_3). A group at the University of Zagreb has shown that CaCO_3 with surface modification provides good bonding to other polymers [7]. The bonding has been achieved largely via electrostatic forces. Our main interest consists in grafting of polymers onto the CaCO_3 surface.

As for the polyester resin morphology, heterogeneous structures have been found: a matrix (bright regions) and interstitial regions dispersed throughout the matrix (dark regions) [8]. The former are microgel polymer particles and consist of several polyester molecules. The dark regions contain: a) nodular subregions due to high crosslinking densities created by strong intramolecular reaction among the pendant C=C bonds of polyester molecules; b) large nodules possibly due to high local styrene monomer concentration; c) interstitial regions containing some unreacted monomers and free polystyrene and polyester chains.

In some applications it is necessary to have the ability of bonding to wet surfaces and PCs have their limitations. An improvement in this respect has been achieved using

for example diacrylate monomers [9]. Often completion of the total polymerization process is not achieved [10] and it is necessary to find alternative methodologies. Both types of problems could be solved by using ionizing energy such as gamma radiation [11, 12].

When applying gamma radiation to polymers, three main processes occur: chain scission, cross-linking and grafting; each one depends on the specific polymer. Gamma radiation makes possible a total and fast cure for certain polymers when the catalyst do not complete their function, eliminating the need for more additives or monomers. Nevertheless, there are limitations, such as excessive rise in the temperature of the polymer due to the high exothermic nature of polymerization. Moreover, the doses required for total cure strongly depend on the composition used; it is necessary to evaluate the rate of cure progress [13 - 15] and the relationship between gelation and vitrification processes which typically occur at the same time [16]. Other advantages of gamma radiation include better solvent resistance of the polymer and its improved form stability with respect to aging and to high temperatures [17].

In curing of polyester resins, free radicals are formed on the chains which react with the double-bonds, and release strain energy (break of the cage), resulting in polymerization. Recovery depends on the chain stress because the radicals provoke high strain. Thus, the recovery probability of the radicals decreases according to the chain stress and the scission of the chemical bond increase. A dependence among the chain lengths, the strain and their rupture has been reported; the shortest lengths have the highest strain energy and they break first [18].

In the present work we have studied the gamma radiation effects on polyester-based polymer concrete, focusing on mechanical improvement. We propose below a novel technology for manufacturing polymer concrete, different from the costly and time consuming current procedures such as chemical attack or thermal treatment. The present work is a part of a larger project on gamma radiation modification of polymeric systems [19 – 21, 12, 6].

Compressive Strength

For non-irradiated PC, the compressive strength increases when increasing the resin concentration, reaching a maximum value of 109 MPa for PC containing 51 % of resin. However, for higher resin concentrations the values go down (Figure 1). Nevertheless, values higher than for the standard polyester + PC (80 MPa) are found, except for specimens containing the resin only.

Consider now effects of gamma radiation on the polyester + PC system, beginning with compressive strength results shown in Figure 2. All composites exhibit values higher than 80 MPa, what means improvements from 50 to 76 %. Interesting is the “periodical” behavior seen in Figure 2 which can be characterized in terms of “stages”. Thus, for 46 % of the resin, four stages are seen: I) from 5 to 10 kGy; II) from 10 to 50 kGy, III) from 50 to 100 kGy; II) from 100 to 150 kGy. First the compressive strength increases when the radiation dose goes from 5 to 10 kGy, reaching a value of 134 MPa. Afterwards, a decrement-increment-decrement behavior is observed. The maximum value is reached (135 MPa) at 100 kGy - a minimal difference with respect to the composite irradiated at 10 kGy.

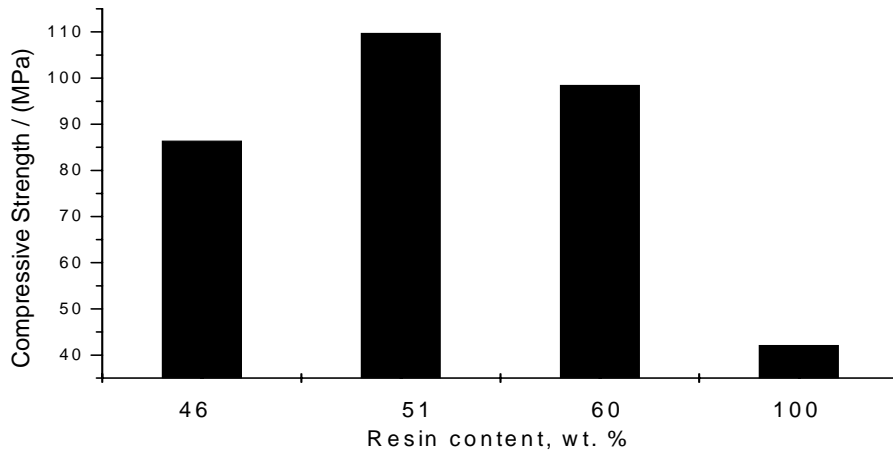


Fig. 1. Compressive strength of non-irradiated polyester + PC composite.

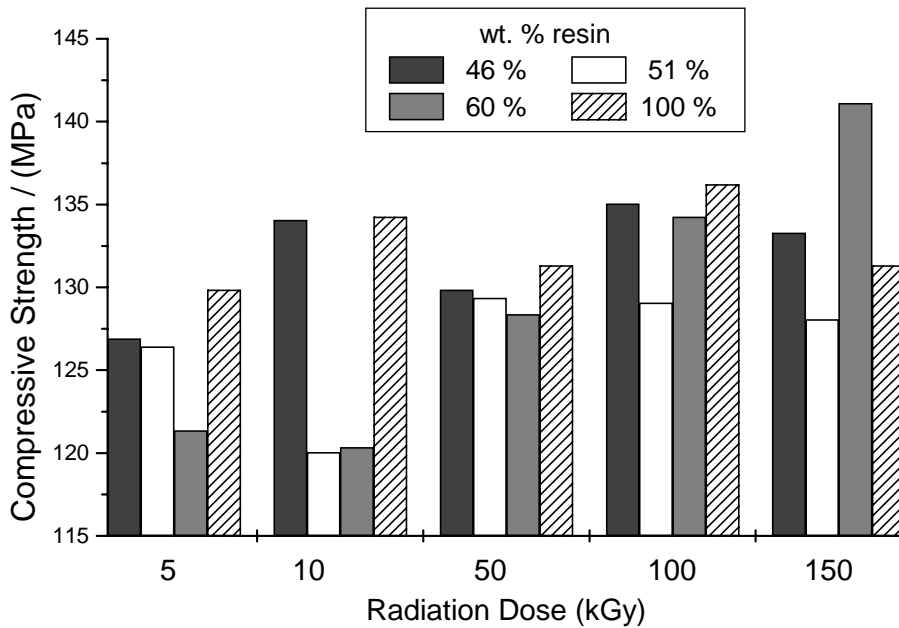


Fig. 2. Compressive strength of irradiated polyester + PC composite at different applied dose.

In the case of the composite with 51 % of the resin we see three well-defined stages: I) from 5 to 10 kGy; II) from 10 to 50 kGy, and III) from 50 to 150 kGy. Now the maximum value is located at 50 kGy. Thus, when increasing the resin concentration, we need a lower radiation dose to reach the maximum values of the compressive strength. There are only small differences in the values at high applied doses, namely 129.3 and 128 MPa for 50 and 100 kGy, respectively. Clearly for economical and time saving reasons it is better to irradiate at low doses.

For the polyester + PC system with 60 % of the resin two well-defined stages are present: I) from 5 to 10 kGy; and II) from 10 to 150 kGy. In the first stage the

compressive strength values decrease when the gamma radiation dose increases; nevertheless for higher doses (above to 10 kGy) the compressive strength increase, showing a linear behavior. For high resin concentration it is necessary to apply high radiation doses to achieve maximum values of the compressive strength. The polyester resin affects the properties more than the calcium carbonate. Consider the compressive strength values for the pure resin (labeled as 100 % in Figure 2) when the radiation dose increases. In the pure resin, four well-defined stages are identified with the maximum value at 100 kGy comparable to the composite with 46 % of the resin. For 150 kGy the values go down, deterioration takes place and now the calcium carbonate assumes the major influence on the compressive strength. Finally, given high compressive strength values found, we infer there is excellent compatibility between the calcium carbonate particles and the resin after irradiation.

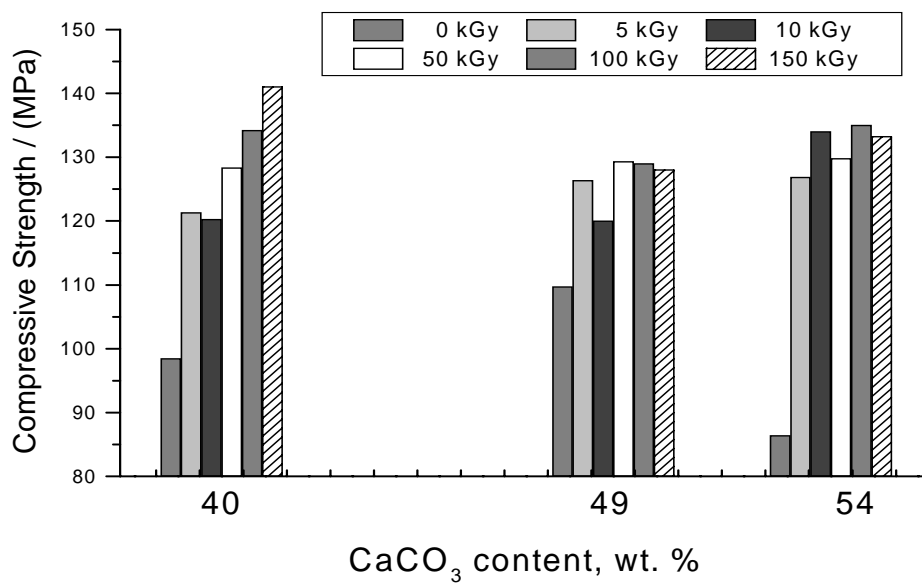


Fig. 3. Compressive strength of irradiated polyester + PC composite as a function of CaCO₃ content.

The compressive strength of the polyester + PC system according to the CaCO₃ content is displayed in Figure 3. Notable is the effect of the gamma radiation in relation to increasing the CaCO₃ content. We consider here two parameters: a) the difference between the maximum and the minimum value for the compressive strength of each irradiated PC; b) the improvement in the compressive strength for each irradiated PC respect to non-irradiated PC. For the first factor, the difference decreases when increasing the CaCO₃ content, that is 20.8, 9.3 and 8.1 MPa for 40, 49 and 54 % of CaCO₃, respectively. Thus, the smallest differences are seen for the highest content of CaCO₃ (54 %); in this case it is better to irradiate the PCs at the lowest dose (5 kGy) instead of the highest one (150 kGy), saving both time and costs. Moreover, the compressive strength values are higher than for the standard for PC (80 MPa).

As for the second parameter, the improvement of the compressive strength does *not* follow the rule: more CaCO₃ content results in more improvement. We have found 43, 17 and 56 % improvement for 40, 49 and 54 % of CaCO₃, respectively. In other

words, at the intermediate CaCO₃ content (49 %) the least improvement is seen. The highest improvement is achieved when the highest CaCO₃ contents is present, namely 54 % of CaCO₃; our best option.

An interesting behavior is observed for 40 % of CaCO₃. The compressive strength also increases when the applied radiation increases. This is not seen at other CaCO₃ concentrations. We infer that a lower content of CaCO₃ allows less interaction between gamma particles and the PC components. Therefore, it is necessary to apply more radiation to achieve high compressive strength values.

Compressive Strain at Yield Point

One of the most important mechanical features of the PC is the maximum strain which make possible - or otherwise - a specific application. Standard strains of 0.01 mm/mm for the polyester + PC reported in the literature are easily exceeded by our irradiated composites; see Figure 4.

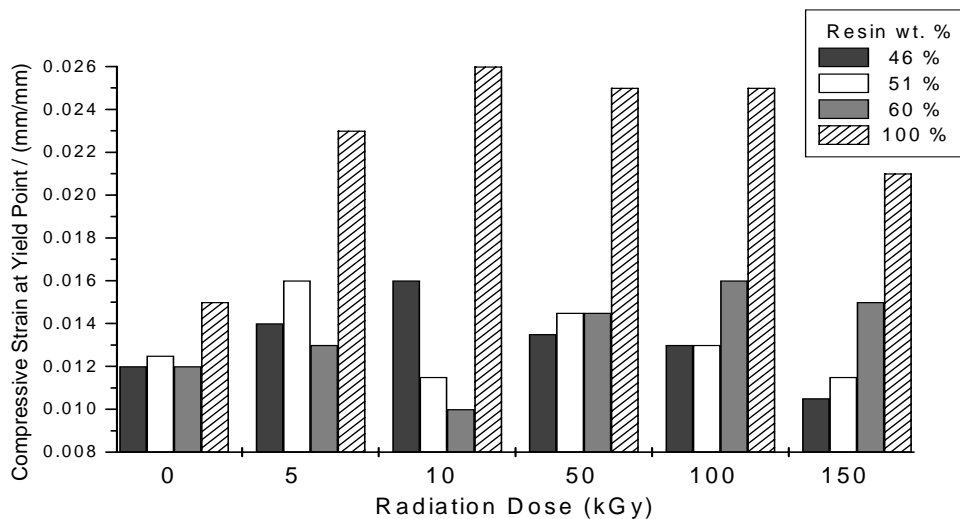


Fig. 4. Compressive strain at yield point of irradiated polyester + PC composite at different applied dose.

In the case of PC containing 46 % of resin, two well-defined stages are present. First the compressive strength increases for the applied dose between zero and 10 kGy. Afterwards, the values go down to 0.01 mm/mm. When increasing the resin concentration to 51 %, the maximum compressive strain value is found at 5 kGy. Also, four stages are present for 60 % resin concentration, but there the highest compressive values are found for high irradiation doses, from 50 to 150 kGy; a maximum is reached at 100 kGy. Clearly it is more convenient to irradiate at 10 kGy than at 100 kGy because the same strain value is reached.

Consider now behavior of the neat resin. There are two stages, first an increase from zero to 10 kGy, where the maximum (for all specimens) is reached at 10 kGy. Afterwards, the compressive strain decreases. We note that all compressive strain values (from 0.015 to 0.026 mm/mm) are higher for the composites. Thus, and as expected, the concrete introduces brittleness [22] which manifests itself in this case in low strain at yield values.

In terms of the CaCO_3 content, the compressive strain values do not follow a simple pattern. We observe that for the highest CaCO_3 contents (54 %) the strain values increase and reach a maximum at 10 kGy. For higher applied doses the values decrease, including the value for 150 kGy which is lower than for non-irradiated PC; nevertheless, all values are higher than 0.01 mm/mm, the standard value for PC. For PC with 49 % of CaCO_3 four stages are detected: I) from 0 to 5 kGy the values increase, II) from 5 to 10 kGy they decrease, III) they increase again from 10 to 50 kGy, and iv) finally they decrease from 50 to 150 kGy. The same number of stages is seen for PC with 40 % of CaCO_3 . We recall that when applying 10 kGy, the lowest values are found in PC with 40 or 49 % of CaCO_3 ; conversely at this dose the highest values are found in PC with 54 %.

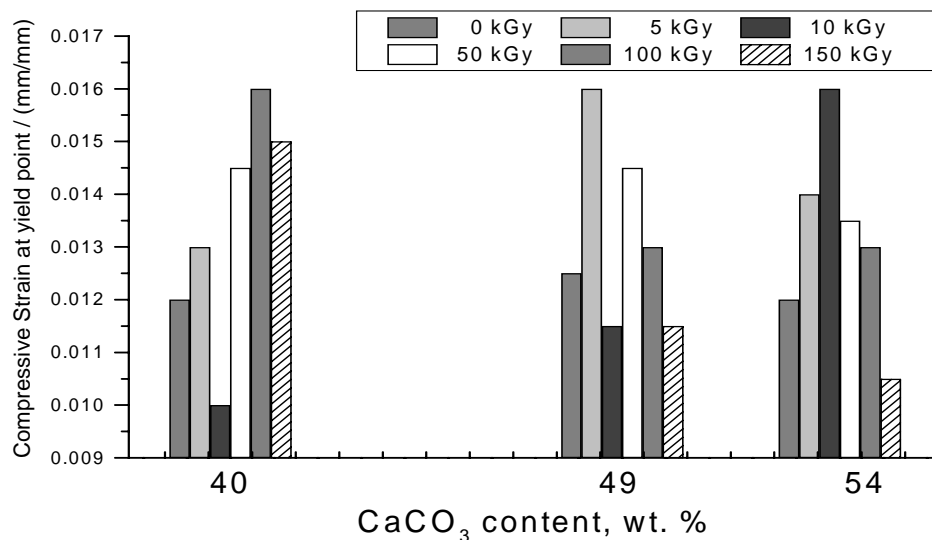


Fig. 5. Compressive strain at yield point of irradiated polyester + PC composite as a function of CaCO_3 content.

Compression Modulus of Elasticity

Another characteristic important for the PCs is the compressive modulus of elasticity E . The results are presented in Figure 6. Except for the non-irradiated samples, the highest E values are found for the lowest resin concentration. There is an optimal concentration of resin for adequate interactions between the CaCO_3 which allows a more elastic behavior; CaCO_3 particles are then surrounded by the polymer matrix.

Once again, a periodical behavior is observed for all resin concentrations, as already seen for the compressive strength and the compressive strain at yield point. At 10 kGy, we see the maximum modulus E value for all irradiated samples. Minimal values are at 50 kGy. For radiation doses above 50 kGy, the compressive modulus of elasticity values are increasing, the composite becomes more and more rigid. CaCO_3 affects the elastic modulus since for the neat resin (labeled as 100 %) the lowest values is seen. A periodical behavior is observed, apparently an intrinsic property of the polyester resins when subjected to gamma radiation. CaCO_3 particles contribute to rigidity.

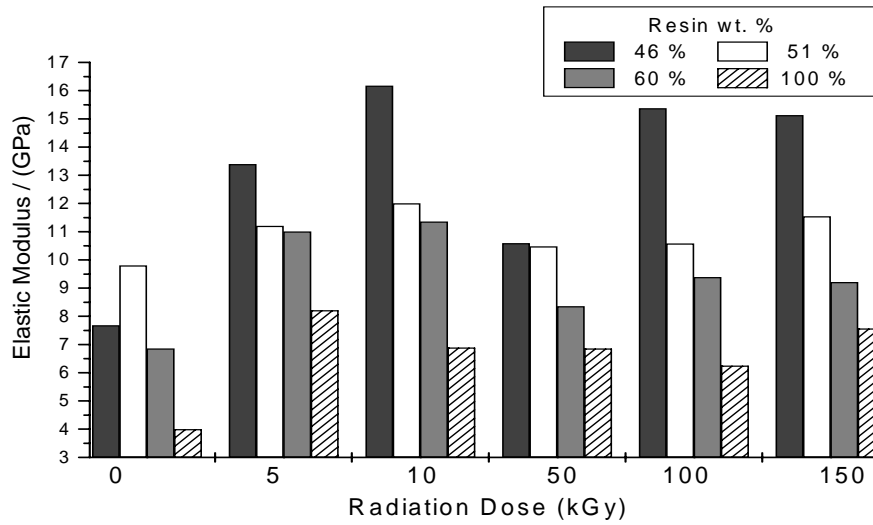


Fig. 6. Compression modulus of elasticity of irradiated polyester + PC composite at a number of applied doses.

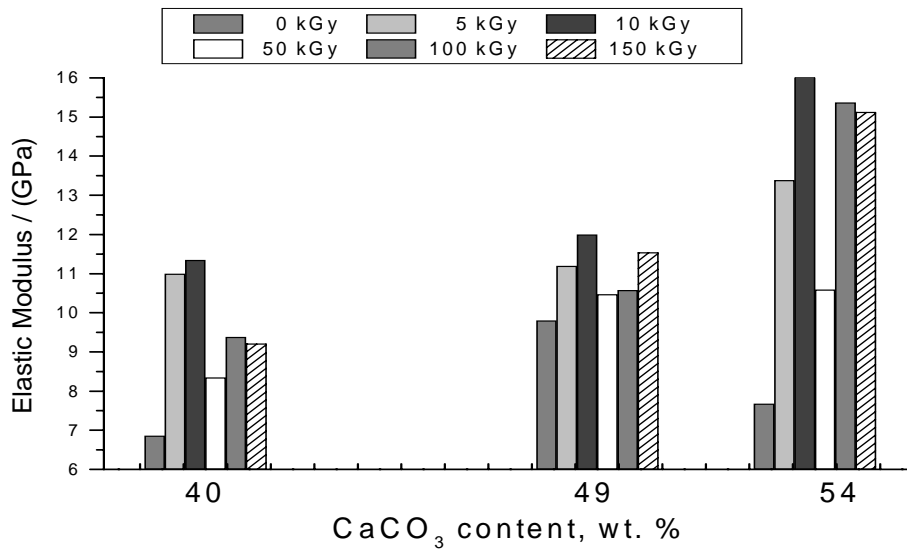


Fig. 7. Compression modulus of elasticity of irradiated polyester + PC composite as a function of CaCO₃ content.

The influence of the CaCO₃ on the compression modulus of elasticity is shown in Figure 7. In general, the increment of the elastic modulus is achieved when increasing at same time both the CaCO₃ content and the radiation dose. This gives a harder material, with E values higher than 6.7 GPa, the standard value for PC. We also observe that for the PCs irradiated at 50 kGy lowest E values are obtained - independently of the CaCO₃ content.

Morphological Analysis

In terms of compressive strength of non-irradiated composites, the maximum values are obtained for 51 % of the resin. For the respective samples the morphology reveals a good distribution of CaCO_3 particles (less than $75 \mu\text{m}$ = mesh: 200) adhered to the polyester resin, that is a strong interaction between CaCO_3 particles and polyester resin; see Figure 8a. When the composite is irradiated at 10 kGy and the lowest compressive strength is obtained, more uniformly dispersed CaCO_3 particles are seen (Figure 8b). The particles are not that well covered by the resin. Thus, the compressive strength and the compressive strain decrease as a consequence of lower adhesion; see again Figures 2 and 4.

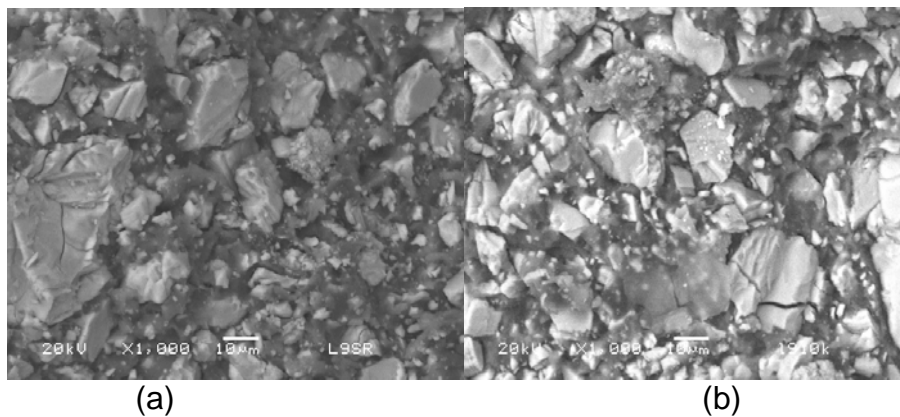


Fig. 8. SEM micrograph of the polyester + PC composite with 51 % of resin: a) non-irradiated, b) irradiated at 10 kGy

On the other hand, we recall that for samples irradiated at 10 kGy, the highest values of the elastic modulus are found (see Figure 9); increasing the resin concentration lowers the elastic modulus. Thus, when adding more solid CaCO_3 particles (Figure 9a), 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 happen when the samples contain less CaCO_3 particles (Figure 9b), and weak interfacial interactions are present.

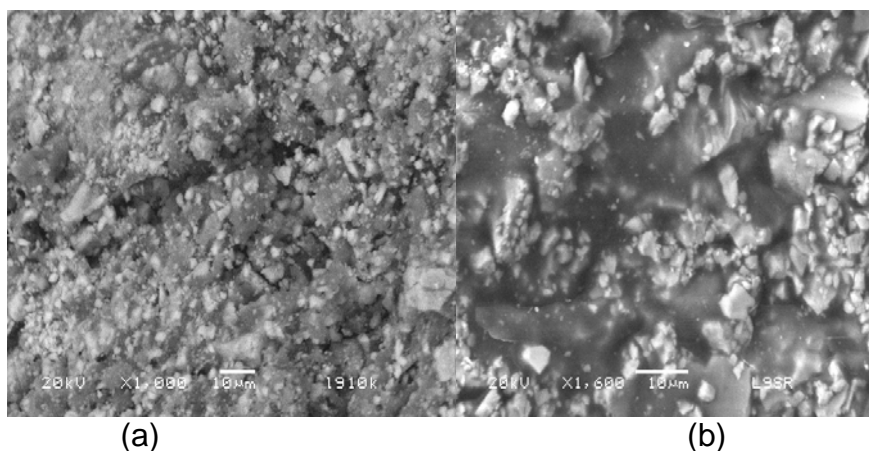


Fig. 9. SEM micrograph of the irradiated polyester + PC composite at 10 kGy: a) 46 % of the resin, b) 60 % of the resin.

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 CaCO_3 surface and the polymer matrix molecules [7].

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. Moreover, a progressive increment of the stiffness of the polyester resin is seen in Figure 10. For non-irradiated resin a smooth surface is observed (Figure 10a). Notable changes occur when a high dose is applied (150 kGy): a rough surface with thin cracks, produced by the scission of the chains (Figure 10b). We emphasize that the resin provides major contributions to the mechanical improvement of the composite. 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.

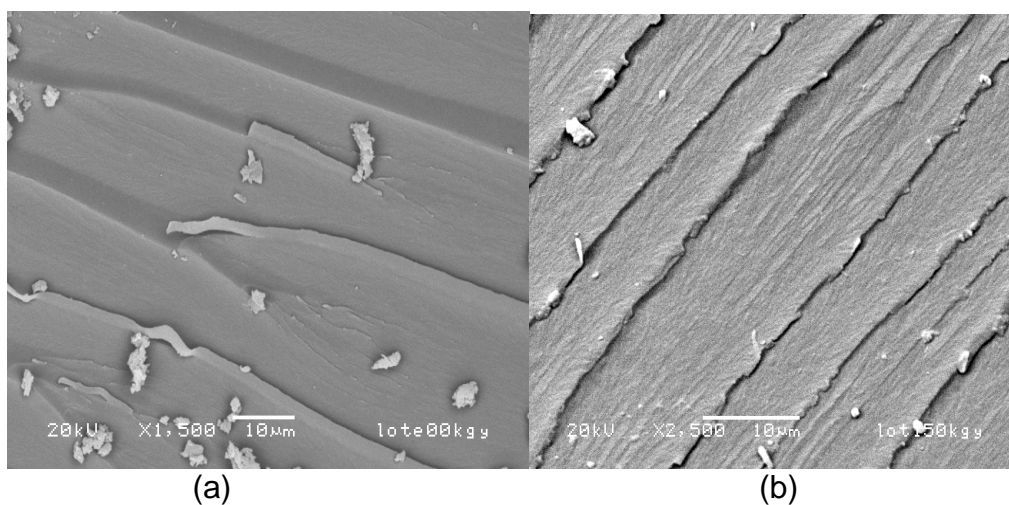


Fig. 10. SEM micrograph of the polyester resin: a) non-irradiated, b) irradiated at 150 kGy.

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 [10]. 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.

Experimental part

Specimen preparation

For preparing the polymer concrete specimens, calcium carbonate (CaCO_3) (0.075 mm: mesh 200) of a local company (GOSATM, Tlalnepantla, Mexico) was used, as well as a commercial unsaturated pre-accelerated polyester resin (orthophtalic): a

viscous liquid resin with a styrene monomer concentration of 30 % (Polylite 32493-00TM, Reichhold, Atlacomulco, Mexico). The proportions of the initiator methyl ethyl ketone peroxide (MEKP) added to the polymer resin for initiating the free-radical polymerization process was of 1 mL/100 g of the resin weight.

Five different polymer concrete lots identified by A, B, C, D, and E were prepared, each one on a different day. The proportions of the polyester resin in the polymer concrete were 46, 51 and 60 % by weight. Also a 100 % polyester resin specimen as reference was prepared. After mixing, the concrete cubic specimens (5 x 5 x 5 cm) were placed in a controlled temperature room at $23.0 \pm 3.0^\circ\text{C}$ up to 72 hours.

Mechanical Tests

Compressive tests of the polymer concrete cubic specimens were carried out in an Instron Universal Testing machine Model 1125 with a charge speed between 91 and 184 kg/s, holding the charge until reaching the maximum value to assure the reliability of the test.

Morphological characterization

The surfaces of the CaCO₃ and polyester resin, before and after irradiation, as well as the fractured zone of the manufactured polymer concrete were analyzed by scanning electron microscopy (SEM) in a JEOL model JSM-5200 machine, in the secondary-electron mode.

Irradiation procedure

The polymer concretes were exposed to varying gamma radiation doses using a ⁶⁰Co source. The experiments were performed in air at the room temperature; the dosages were 5, 10, 50, 100 and 150 kGy at the dose rate of 6.1 kGy/h. The irradiation was provided by a 651 PT Gammabeam Irradiator manufactured by the Atomic Energy of Canada Ltd. (AECL, Chalk River, Ontario), and located at the Institute of Nuclear Sciences of the National Autonomous University of Mexico.

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