1. Introduction

A large variety of concretes is based on a variety of cements [1–3]. Mineral concretes – used for a very long time – typically contain structural defects, including delaminations and voids. Polymer concretes (PCs) with a polymeric resin matrix have better mechanical properties than mineral concrete. Thus, PCs are used to make reinforced slabs, overlays for highway pavements and bridge decks, pipe coatings – as well as in repairing deteriorated mineral concretes (Portland cement concrete).

The key criteria for usability of a concrete for a specific application are compression strength $\sigma_c$ and compressive strain at yield point $\varepsilon_Y$. While PCs have these parameters better than mineral concretes, in potential applications still better values of $\sigma_c$ and $\varepsilon_Y$ than those presently available are required. At least three options deserve consideration:

a) Use of fibers for reinforcement. There is a large variety of reinforcements for polymeric matrices [4–6]. The work of San-Jose et al. suggests using fibers or other objects with irregular shapes and large sizes since the adhesion between the reinforcement and the matrix depends on the physical interactions between them [7]. Similarly, elongated objects provide more improvement of mechanical properties than spherical ones [8]. This should not be surprising; Kopczynska and Ehrenstein [9] discuss how interfaces largely determine properties of multiphase materials.

b) Use of small particles as a dispersed phase. Special attention to the shape, size and number of...
aggregates is needed because the aggregates act as stress concentration points. Some PCs contain only one aggregate, others more than one, such as a PC with quartz fine sand, quartz gravel, quartz powder and chalk [7]. Moreover, the interface surface area can be enhanced by decreasing the size of the aggregate particles (inclusive to nano-dimensions), so as to produce strong cohesion; undesirable agglomeration of the particles has to be avoided. The Zagreb group has shown that CaCO$_3$ with surface modification provides stronger bonding to polymers largely via electrostatic forces; moreover, CaCO$_3$ without pre-treatment provides stronger interfacial adhesion than after a treatment [10]. An improvement of the attraction between the polymer and the aggregates can also be achieved by adding a coupling agent such as silane to the monomer. This lowers the extent of pore formation and causes a decrement in stiffness [11]. Our main interest consists in grafting polymers onto aggregates surfaces. c) Irradiation – by a variety of sources [12–19]. Gamma irradiation has several advantages over conventional curing processes: I) no catalyst or additives are needed to initiate the reaction; II) the initiation is homogeneous throughout the system; III) it can be performed at any temperature and be interrupted at a chosen reaction time; IV) the polymer can be analyzed at selected reaction stages; and V) the temperature during reaction initialization is maintained – as contrasted with highly exothermic curing without irradiation. Moreover, the gamma irradiation applied to polymers causes three different processes: chain scission, crosslinking or grafting. Which of these processes prevails depends on the nature of irradiation, chemical nature of the polymer and the applied dose [20]. In this situation we have investigated a PC containing an unsaturated polyester resin, CaCO$_3$ and silica sand – with inclusion of polyester fibers and gamma irradiation for their further reinforcement.

2. Materials and procedures

Our PC specimens consist of natural silica, calcium carbonate (GOSA™, Atizapan, Mexico), and a commercial unsaturated pre-accelerated orthophthalic polyester resin, a viscous liquid with 30% styrene monomer (Polylite 32493-00™, Reichhold, Atlacomulco, Mexico). Methyl ethyl ketone peroxide is the initiator of free-radical polymerization (1 ml/100 g polyester). The sizes of silica sand particles were of 150, 212 and 355 μm (mesh 100, 70 and 45, respectively), and for CaCO$_3$ particles 75 μm (mesh 200). The standard mixing procedure according to the ASTM C305 was followed. It consists of two stages, mixing for 1.0 minutes at the paddle speed of 140 rpm, and followed by a total of 1.5 minutes at the speed of 285 rpm. The compositions of PCs are summarized in Table 1. After mixing, PC cubic specimens with the side of 5.0 cm were kept at 23.0±3.0°C for 72 hours. Six different lots were elaborated (labeled I to VI) on different days, each one containing 15 samples. That is, for each type of PC (see Table 1) 15 concrete specimens were made. For obtaining fiber-containing PCs, we have also followed the ASTM C305 mixing method, adding in the two stages the polyester fibers (Gütermann Polygal, Cuernavaca, Mexico) with diameters between 30 and 40 μm and 20 mm long. The compositions of PCs with fibers are listed in Table 2. Three different lots were elaborated (labeled VII to IX) on different days, each one contained 15 samples. That is, for each polyester-fiber content 15 concrete specimens were made. The PC specimens were subjected to gamma irradiation using a 60Co source at five different dosages: 0, 5, 10, 50 and 100 kGy at the rate of 2.48 kGy/h in air at room temperature. For comparison analysis, polyester fibers alone were irradiated under the same conditions, in packets of 50 fibers in a capillarity tube. The source was a 651 PT Gammabeam Irradiator, manufactured by Atomic Energy of Canada Ltd. (now NORDION, Chalk River,

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<tr>
<th>Specimen (type)</th>
<th>Polyester resin [wt%]</th>
<th>CaCO$_3$ [wt%]</th>
<th>Silica sand [wt%]</th>
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<tbody>
<tr>
<td>I</td>
<td>20</td>
<td>5</td>
<td>75</td>
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<td>II</td>
<td>20</td>
<td>12</td>
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<td>III</td>
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<td>V</td>
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<td>50</td>
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<td>VI</td>
<td>20</td>
<td>60</td>
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<tr>
<th>Specimen</th>
<th>Polyester resin [wt%]</th>
<th>CaCO$_3$ [wt%]</th>
<th>Silica sand [wt%]</th>
<th>Polyester fiber [wt%]</th>
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<tbody>
<tr>
<td>VII</td>
<td>20.0</td>
<td>60.0</td>
<td>19.90</td>
<td>0.10</td>
</tr>
<tr>
<td>VIII</td>
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<td>60.0</td>
<td>19.75</td>
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</tr>
<tr>
<td>IX</td>
<td>20.0</td>
<td>60.0</td>
<td>19.60</td>
<td>0.40</td>
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Ontario), and located at the Institute of Nuclear Sciences of the National Autonomous University of Mexico.

Compressive strength testing was performed in an Instron Universal Testing machine Model 1125, according to the ASTM C-109M standard. The charge speed used was of 120 kg/s, holding the charge until reaching the maximum value to assure the test reliability.

3. Compression strength

In Figure 1 we show the compressive strength values $\sigma_c$ for PCs without fibers. For non-irradiated PCs, $\sigma_c$ values increase according to the CaCO$_3$ and silica sand concentrations; the lowest increment is seen for PC type I and the highest for PC type VI (see Table 1). That is, the compressive strength values increase when increasing CaCO$_3$ and decreasing silica sand concentration at the same time. The compressive strength values vary from 74 to 107 MPa.

Similar behavior is seen in irradiated PCs, with the values varying from 85 to 122 MPa. The highest value of 122 MPa is achieved for PC type V (50/30 CaCO$_3$/silica sand wt% ratio), irradiated at 100 kGy. This result constitutes an improvement of 64% with respect to the minimum value obtained for non-irradiated PC type I.

The next step was evaluation of effects of polyester fibers incorporation into the PC. We have chosen those PCs in which variations in the compressive strength values were minimal. Thus, PC type VI was selected (see Figure 1) since the differences did not exceed 8%.

The results for polyester-fiber PCs are shown in Figure 2. The $\sigma_c$ values in non-irradiated samples are lowered by introduction of the fibers. However and as expected, $\sigma_c$ values depend on a combination of the fiber concentration and the applied radiation. By following the fiber concentrations, a different behavior is seen. For PCs with 0.1 wt% of fiber, the compressive strength values increase along with increasing applied radiation dose. For 0.25 wt%, the compressive strength increases up to 10 kGy, then it decreases at 50 kGy, and finally it increases again at 100 kGy; for 0.4 wt%, the highest value is seen at 5 kGy. In this sense, we can describe this $\sigma_c$ behavior as periodic. More notable is the periodicity if a fixed radiation dose is followed.

For fiber-PCs, the highest $\sigma_c$ value is seen for 0.1 wt% fibers and 100 kGy of radiation dose. Recall that in Figure 1 the highest overall $\sigma_c$ value is also for 100 kGy. This can be related to effects of irradiation on polyester resins reported by Jurkin and Pucić [18]. At 5 kGy the irradiated polyester resin abruptly changes from a viscous liquid into a hard thermoset solid (3-D network), reducing the polymer chains mobility [18] – what enhances $\sigma_c$. Between 5 and 50 kGy, the changes can be attributed to behavior of the fibers since the polyester resin retains its dimensional stability. For doses exceeding 50 kGy, the polyester resin begins to deteriorate [18] and lower $\sigma_c$ values are seen.

As said, the $\sigma_c$ values go from 74 to 107 MPa for non-irradiated PCs when varying the CaCO$_3$ and silica sand concentration; the respective range for irradiated PCs is 85–122 MPa. We recall in this context also earlier results for the same polyester resin containing whether CaCO$_3$ or silica sand. The present results are lower than those reported for PCs containing only CaCO$_3$ (from 127 to 135 MPa) [21], but higher than those obtained using silica sand only (from 62 to 68 MPa) [22]. Thus, in irradi-
ated materials CaCO₃ particles support more compression strength than the silica sand particles. Changes on surfaces of irradiated polyester fibers were observed by scanning electron microscopy (SEM). First the fibers were vacuum-coated with carbon (3–10 nm thickness) in a vacuum pump at 50 mTorr. A JEOL model JSM-5200 was used in the secondary electron mode. For non-irradiated fibers smooth and homogeneous surfaces are seen (Figure 3a). For 10 kGy several ‘particles’ are observed on the fiber surface (Figure 3b). At 100 kGy, SEM reveals more such particles (Figure 3c). Apparently irradiation causes a fractional degradation of the fiber surfaces – manifested as formation of the ‘particles’.

Chain scission results in formation of low molecular weight chains at higher doses, providing more contact points and thus improving physical adhesion between the fibers and the concrete. As one of the consequences, the concrete will resist larger loads by inclined forces – oriented at some angles relative to the longitudinal axes of the fibers.

4. Compressive strain at yield point

We now turn to the compressive strain at yield point $\varepsilon_Y$ results. For non-irradiated PCs we see three well defined stages: increment-decrement-increment associated with CaCO₃ and silica sand concentration (Figure 4). This periodic behavior seems to be the result of a competition between two reinforcing components, CaCO₃ and silica sand. For irradiated PCs two different types of behavior are seen: I) three well-defined stages, with a increment-decrement-increment sequence – observed only in PCs irradiated at 5 kGy, II) two stages, with a decrement-increment sequence, observed in PCs irradiated at 10, 50 and 100 kGy. The values for irradiated and non-irradiated PCs vary from 0.007 to 0.017 mm/mm. Apparently, the strain is supported by the polyester resin – a polymeric material - more than by mineral components CaCO₃ and silica sand.

The highest values for PCs without fibers are seen for PC type VI (20/60/20 resin/CaCO₃/silica ratio). Thus, this material was chosen as a convenient reference material for evaluation of effects of gamma
irradiation after addition of polyester fibers. The addition of the fibers, even only 0.1%, increases $\varepsilon_Y$ tremendously, see Figure 5. The compressive strain values for fiber-PCs ranging from 0.025 to 0.047 mm/mm are higher than standard values reported in the literature for polyester-based PC (0.010 mm/mm) [20]. We note improvements from 47 to 176% with respect to conventional PCs (without fibers and non-irradiated).

We recall that the materials brittleness $B$ is inversely proportional to $\varepsilon_Y$ [23, 24]. If the dynamic storage modulus $E'$ values ($E'$ also appears in the definition of $B$) are comparable, our materials with higher $\varepsilon_Y$ values are less brittle. Thus, irradiation of fibers causes material softening, and they sustain the compressive strain much more than the polyester resin.

Compare now our $\varepsilon_Y$ range of 0.025–0.047 mm/mm with results for PCs with the same polyester resin but containing one mineral, such as PC with CaCO$_3$ (0.01–0.016 mm/mm [21]) or with silica sand (0.006–0.013 mm/mm [22]); we conclude that a combination of two different minerals and one kind of polymeric fibers result in higher compressive strain values that in PCs containing one mineral.

5. Compression modulus of elasticity

In Figure 6 we show values of the compression modulus of elasticity $E_c$ for PCs without fibers. Also here periodic behavior is seen. For non-irradiated PCs the values range from 5.4 to 8.9 GPa, thus higher than our result for pure polyester resin, $E_c = 3.9$ GPa [20]; as expected, adding the minerals increases $E_c$.

Consider now $E_c$ values for irradiated PCs. There is a large variety of behavior, no general pattern; the $E_c$ ranging from 8.6 to 17.4 GPa which are higher than values reported for polyester-based PCs (6.7 GPa) [22]. The highest value is for PC with 5% of CaCO$_3$ and 75% of silica sand irradiated at 5 kGy. This means an improvement of 159% respect to standard value reported in the literature [22]. The addition of polyester fibers lowers $E_c$ dramatically (results not included here for brevity). Both irradiated and non-irradiated PCs have results in the range from 3.1 to 3.7 GPa. Hence, the addition of the fibers increases ductility.

We have obtained notable improvements in the compressive strength and compressive strain at yield point – a consequence of contributions of irradiation, two aggregates (CaCO$_3$ and silica sand) as well as polyester fibers. Such behavior is not seen in polyester-based PCs with one aggregate.

Acknowledgements

Financial support by the National Council of Science and Technology of Mexico (CONACyT), Mexico City (Grant # 49899/2005) and by Hispanic and Global Studies Initiatives Fund of the University of North Texas, Denton, are acknowledged.

References