

POLYMER CONCRETES: A DESCRIPTION AND METHODS FOR MODIFICATION AND IMPROVEMENT

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ABSTRACT

Portland cement concrete (PCC) has been successful in many applications. However, since the 1960s technological investigations concerning modifications of concrete by polymeric materials have been conducted. Attention has been focused on concretes in which the continuous phase is some kind of polymeric resin and the discrete phase is some type of mineral aggregate. Such composite materials are known as Polymer concrete (PCt) and boast several advantages such as higher strength and a shorter curing process. In spite of these advantages, there are deficiencies that could be addressed by fiber incorporation into PCts, however this kind of approach is not typical. Here we acquaint readers with the nature of polymer concretes as these materials have not yet gained wide recognition. We describe recent developments regarding the influence of fiber reinforcements on PCts. The curing process is a critical concern in dealing with polymer concretes as it is with Portland cement concrete. Studies on the effects of gamma ionizing radiation on the curing process and on final properties of PCts are ongoing. Developments in this area are also described here. In particular, the effects of gamma irradiation on the mechanical properties are discussed. Notably, improvements of the Young's modulus E described here have wider implications and may be indicative of improvements or modifications to other properties not directly tested. Specifically, the modifications to the Young's modulus can be a defining measure of whether one will obtain a ductile or more brittle concrete.

Keywords: *Gamma radiation, polymer concrete, mechanical properties*

1. INTRODUCTION

In the field of Materials Science and Engineering (MSE) cement and concrete have been familiar materials from the start.

Throughout the 1900s scientific investigation further elaborated the details of mechanisms and properties associated with concrete, especially of Portland cement concrete (PCC). Thus, a discussion of the nature of such mineral

concretes is no stranger in textbooks on materials science. Polymer concrete (PCt), by contrast, was developed only about 50 years ago and remains a relatively unknown entity in MSE. Advancements in the development and knowledge of polymer concretes have been gradual, but more recently significant strides have been made. While PCts can offer many advantages over mineral concretes, they not surprisingly bring some challenges as well. The matter of reinforcing PCts is one point of development. There are few firmly established principles regarding fiber reinforcement of PCts. Also, the process of curing is central to the design and use of polymer concrete. Environmental factors are critical to PCt curing. The aim of this article is to describe the nature of polymer concretes, discuss fiber reinforcement of PCts, and describe certain effects of irradiation on the curing process. In preparation for defining polymeric concretes, we first discuss the familiar mineral concretes as a point of comparison.

2. MINERAL vs. POLYMERIC CONCRETES

Ordinary Portland cement concrete 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 immobilization¹. 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. The special role of particle packing to achieve optimal properties of cements and concretes is discussed at length by Roy and co-authors². While newly poured PCC sets within hours or days, the curing process may not be complete for several years. Mindess has written in this journal an excellent description of

mineral concrete materials, including discussion of composition, properties, applications, and testing³. Around the world PCC is regarded for its high strength and insulating capability, among other characteristics. Nevertheless, PCC has several limitations, including low tensile strength, poor environmental durability (resistance to freeze-thaw), and susceptibility to sulfate and acid attack. To solve these problems, various approaches have been tried, for example: a) reinforcement with different materials (fibers, particles, rods, etc.); b) design of special cements to avoid sulfate attack; c) protective coatings placed on concrete exposed to acids⁴. Concrete is considered a brittle material, and compared to polymers has lower flexural strength and toughness⁵.

Mineral concretes are not limited to PCC. Recent work has been done to develop cements based on magnesium oxide and magnesium sulfate to replace the Portland cement in concrete⁶. These materials are being developed primarily to reduce the emission of carbon dioxide in concrete production. Likewise geopolymers are considered friendly to the environment. In early attempts to produce concretes with exceptionally high strength, geopolymers were utilized. The development of geopolymers and their successful commercialization as the geopolymer concrete PYRAMENT® is described by Davidovits⁷ (who pioneered the development and also coined the term geopolymer). Geopolymers are essentially polysialates: amorphous to semicrystalline silico-aluminate structures. As early as fall 1993 PYRAMENT concrete was used in more than 50 industrial facilities, in military installations in the US and other countries, and in non-military airports⁷. PYRAMENT sets in about 4 hours and was noted for its high early strength and higher ultimate strength compared to PCC. Geopolymers could be considered one example of a broader class of inorganic polymers. Many such materials can provide similar performance to traditional cementitious binders⁸. However, in spite of many advantageous properties, inorganic polymers are not a universal solution for all material selection problems; instead they

can be thought of as a candidate to incorporate into the mix and process design for optimization in a given application⁸.

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 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 PCt we have a polymeric matrix as the continuous phase and dispersed inorganic particles as a discrete phase.

Typically PCt 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^{9,10}. Moreover, they exhibit good creep resistance¹¹, 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 PCts with increased capillary diffusion of solutions, which weakens the bond between the aggregate and the matrix¹².

PCts have a variety of applications: a) in highway pavements; b) as underground wastewater pipes; c) for manufacturing thin overlays (since it has the advantage of providing light weight and also because PCt does not produce bleed water [water that emerges from concrete that has been prepared with excess water]); d) as precast components for bridge panels, overlay bridge decks, parking garage decks, industrial floors and dams,

buildings, machine bases and transportation components as well as for hydraulic structures such as dams, dikes, reservoirs and piers (where PC creates a highly abrasion-resistant surface)¹¹; e) in high pressure and temperature environments, such as the utilization of geothermal energy, due to its durability in hot acidic springs; f) for repair of structures and for coatings because of its strong bonding with PCC (there must be no sealants, curing compounds, or any other material covering the concrete, as it will interfere with the adhesion of PCt). Acrylic latex modified concrete mixtures are specifically formulated for thin coatings and concrete restoration¹¹.

In some applications where it is necessary to have the ability to bond to a wet surface, PCt has limitations. A few types of monomers have been used with limited success, for example diacrylate monomers¹¹. However, in general (not just in a wet setting), the polymerization (meaning conversion of monomer to polymer) is not complete for the type of thermoset resins used in PCts¹³. It is therefore necessary to find alternative methodologies for such processes.

PCt properties depend on the interactions at the interface between the polymeric binder (i.e. thermoset resin) and the mineral aggregate. Furthermore, like PCC, PCt exhibits some brittle characteristics¹⁴ that have limited its usefulness in load-bearing applications. Therefore improving its toughness and post-peak stress-strain behavior are necessary; these parameters are also essential features to evaluate the performance of the material for impact, earthquake, and fatigue loading^{15,16}. Hence developing better PCt systems and also characterizing the mechanical features of PCts in terms of their constituent materials are essential for efficient utilization of PCts in real applications^{12,17}.

3. FORMULATIONS

In its manufacture, PCt requires care in the casting process, attention to curing temperature, composition, and careful choice in type of

resins and aggregates. The latter involve several linked characteristics: specific area, interfaces with the matrix, strength and deformability, shape and size. For example aggregates with irregular shapes and high surface area improve the anchorage with the matrix¹⁸.

The proportion of thermosetting resin to aggregate as well as different types of aggregate varies in different formulations of PCt. In principle, the mix design of PCt typically involves an aggregate size gradation to provide the lowest possible void volume that will require the minimum polymeric binder concentration necessary to coat the aggregates and to fill the voids¹². Several different formulations for PCts are described in Table 1.

Different formulations of PC have been developed as described in Table 1.

Table 1. Different PCt formulations.

(Sand type abbreviations: S = Silica, F = Foundry, B = Blasting)

Ref. *	Epoxy Resin (wt.%)	Poly-ester resin (wt.%)	Sand (wt.%) (type)	Catalyst (MEKP) (wt.%)
19	20	---	78.5 (S)	1.5
21	20	---	78.0 (F)	2.0
20	---	10	88.5 (B)	1.5
20	---	15	83.5 (B)	1.5
20	---	18	80.5 (B)	1.5
12	---	20	77.5 (S)	2.5
21	---	20	78.0 (F)	2.0

* Data in this table come from several sources. Numbers in this column indicate bibliographic references [Ref.].

4. AGGREGATES

A variety of aggregate types have been used in PCt: silicates, gravel, limestone, calcareous rock, granite, clay, quartz, crushed stone, silica sand or calcium carbonate (CaCO_3)^{22,23}, as well as fine fly ash, phosphor-gypsum, cinder and silica fume (SUF).

Several silica sands have been used in the foundry industry; they are listed in the following table.

Table 2. Types of silica used as aggregate.

Sand Type	Grain size range (mm) *
Foundry 6/16	2.36 - 0.85
Foundry 16/24	1.0 - 0.5
Foundry 110	1.0 - 0.063
Blasting	0.85 - 0.60
Quartz (Foundry use)	5 - 0.075
Quartz	0.425 - 0.30
Silica	5 - 0.60

* Data come from several sources^{11,12,14,24}.

As stated earlier, the mix design of PCt typically uses an aggregate size gradation to provide the lowest possible void volume and require the least polymeric binder necessary to coat the aggregates. One such combination is PCt with 15 wt. % of resin and 85 wt. % of siliceous sand with grain sizes of 245 μm or 342 μm ^{16,21}. Sometimes, the sand in a given PCt has different grain sizes, for example: (a) 1350 μm (60 %); 120 μm (30 %), and 670 μm (10 %) (as percentages of total aggregate)¹⁴; or (b) 850 μm (23 %), 425 μm (10.2 %) and 90 μm (6.1 %) (as percentages of the whole material)²⁵.

Other PCts contain more than one type of aggregate. Some examples: PCt with polyester resin (85-95 wt. %) and (the remaining 5 to 15 %) inert inorganic filler composed by silica sand (88 %) and silica flour (12 %); or PCt with orthophthalic polyester resin (12.3 %) and quartz fine sand (24.7 %), quartz gravel (49.3 %), quartz powder (6.7 %) and chalk (7 %). With these formulations higher values of mechanical performance have been obtained with respect to the standard values of: 90 MPa for compressive strength, 30.4 GPa for Young modulus and 5 % of maximum strain¹⁸.

Diminution of particles' size to nano-dimensions produces strong cohesion so the extent of aggregation is increased. For example CaCO_3 nanofillers with particle sizes around 20

nm and specific surface area of 70 m²/g develop aggregates ranging from 0.1 to 13 μm²⁶ (<15 μm is desirable).

Mineral aggregates and incorporated fibers may undergo prior processing. For example chopped glass fibers may be soaked in a 2% silane aqueous solution (γ-methacryloxy – propyltrimethoxy - silane, γ-MPS). The effects of silane modification are influenced by several factors, including: the specific surface area of the filler, alkoxy- and organo- functionality of the silane, type of solvent, pH of the aqueous slurry, and conditions during the modification process²⁶. When surface-modified aggregates are added to polyester PCt, mechanical performance is improved compared to that of unmodified PCt; for instance increases of 14% in the compressive strength, 35% in the tensile strength, and 50% in flexural strength are observed; the compressive, tensile and flexural values for unmodified PCts are 102, 9 and 10 MPa, respectively^{20,25}. In the same analysis, there was no significant change in the compressive elastic modulus.

5. RESINS

The main resins used for manufacturing PCt, are: (1) polyester resins that resist mild corrodents and non-oxidizing mineral acids; (2) isophthalic polyester resins; (3) resins based on bisphenol-A; (4) orthophthalic polyester resins¹⁹; (5) epoxy resins, and (6) vinyl ester resins. The polyester resins are the most common due to their low prices and corrosion resistance.

Like Portland cement concrete, polymer concretes must be cured, although the mechanisms underlying the two processes are different. Curing of polyester resins must be well controlled in order to obtain good workability for the highly viscous PCt specimen and to avoid the presence of water, which can damage the hardening process of the resin^{12,19}. During the curing process, polymer chains are formed from the monomer resin. Not only do the monomers combine in chains but

the chains also connect with each other in a process referred to as crosslinking²⁸. In the first stage of polymerization (i.e. curing process), the resin is usually in the liquid state. Once the reaction temperature is reached, the physical state of the compound changes abruptly from liquid to gel and the crosslinking reaction slows down.

For polyester resins, the curing reaction proceeds by free-radical polymerization. Different initiators and promoters have been used to catalyze the process. For example, methyl ethyl ketone peroxide (MEKP), amine or benzoyl peroxide (BZP) as initiators, and cobalt naphthenate or dimethyl-para-toluidine (DMPT) as promoters, with weight percentages dependent on the resin content²⁷.

6. FIBER REINFORCEMENT

Fiber reinforced composites (FRC) have a reputation for being superior in their stiffness, strength, and creep resistance. A variety of FRC systems have been developed for specific applications such as in structural civil engineering, automotive applications, and high temperature corrosive environments. Nevertheless, *there is very limited information on fiber-reinforced PCt systems*. Thus substantial experience and broad knowledge on the optimal compositions, properties, and stress-strain relationships are needed, especially with respect to design, production, and quality control. By contrast, the use of fibers to increase flexural strength, fatigue resistance, toughness and ductility of mineral cement-based materials has been well established, while studies are ongoing for fiber reinforced PCC 5.

A basic laboratory procedure to determine the fiber volume content, longitudinal and transverse moduli, and elastic modulus (at various angles) of fiber reinforced composites has been described²⁹. For polymer concretes in particular, natural or synthetic fibers – such as carbon or glass fibers – can be added to the PCt matrix to improve the mechanical performance. Glass fibers are non-corrosive, non-conductive,

and non-magnetic and offer low density and high modulus¹⁹. Mechanical improvement depends on the fiber type and on its concentration in the PCt²⁹. For example glass and organic fibers have little effect on the pre-cracking behavior but do substantially enhance the post-cracking response, which leads not only to improved toughness and ductility but also to higher tensile, flexural and impact strength.

A special case of fiber reinforcement is the addition of oriented fibers. Reinforcement glass fibers and plastic bars placed along the principal stress directions reduce the creep deformation, which if present to a large degree might result in an impaired structure or even cause structural collapse. Moreover, the composite can sustain loads for long periods of time²⁷. For unidirectional composites, changes in the tensile strength by addition of fibers are influenced by several parameters such as: length and number of fibers; constituent material properties including interface; and microstructural features (volume fraction and arrangement of the fiber)³¹. The current knowledge about effects of fiber reinforcement (with random distribution, not unidirectional) on strength of several specific types of polymer concretes is summarized as follows:

a) For polyester PCt with fiber glass reinforcement, the compressive strength values depend on the percentage of polyester resin in the mix and the concentration of fiber glass. For each resin content, there is an optimal fiber content (based on maximum strength). Values of the modulus of elasticity in compression (ϵ) decrease when the fiber content increases. On the other hand, there is an increase in ϵ with increasing polyester resin content. With respect to the failure strain property, values increase when the glass fiber content increases. For PCt with 10 % polyester resin content, failure strain goes from 0.013 to 0.024 mm/mm as fiber content increases from 0 to 6 vol. %.

b) For polyester PCt, improvement of 95 % in the flexural strength has been obtained when adding 2 % of glass fibers and using silane as

coupling agent¹⁶;

c) For epoxy PCts with epoxy resin concentration varying from 10 to 18 wt. %, both the flexural strength and the fracture behavior have been improved by adding 2, 4 or 6 wt. % of chopped glass fibers (with no sizing and soaked in a 2 % silane solution).

d) When compared to commercial concretes, plain epoxy concrete exhibits higher compressive strength, with values ranging from 17 to 33 % higher. The values increase further when fibers are added, for instance from 27 to 45 % higher for glass-fiber reinforced concretes or from 36 to 55 % higher for carbon-fiber reinforced epoxy concretes than for PCC.

Fiber reinforcement of PCts affects strength (compressive and flexural) differently than it does elastic modulus. Neither carbon-fiber nor glass-fiber reinforcements improve the compressive elastic modulus; in fact, a slight decrease is observed in carbon fiber reinforced composites. Meanwhile, the values of Poisson's ratio do not show a clear trend¹⁶. Owing to the random distribution of fibers this anisotropic feature has its value averaged through all possible orientations.

Up to now we have discussed mostly glass and carbon fibers. Another important class of synthetic fibers is the polyamides (nylon), whose commercial success is due to generally outstanding properties. Moreover polyamides are an economically attractive material, as well. Small amounts of nylon fibers substantially improve the impact resistance of composites. The improvement results from stretching and pulling-out of the fibers, which occurs after failure of the matrix and at a lower load and large strains. Nevertheless, the added fibers have very little effect on tensile or bending strength, and it would be advantageous if composites could be designed to support an increasing load after the cracking of the matrix³².

Polypropylene fibers (PP) are chemically inert, have a hydrophobic surface, and exhibit good to

fair water resistance and good alkali resistance. Moreover, they are currently manufactured in a variety of geometries and configurations and can be produced as monofilaments, collated fibrillated fiber bundles, or continuous films. Presently there is little established data regarding PCTs with PP fibers. This is in contrast to a large amount of information on such fiber-reinforced PCCs.

In some composites, chemical bonding (sometimes referred to as elastic bonding) between the fiber and matrix is not strong compared to frictional resistance against pull-out along the debonded segment³³. In addition, most fiber deformation processes lead to local mechanical interactions between fiber and matrix and, therefore, may be regarded as a macroscopic "roughening" effect. In the case of nylon fibers, the pull-out process can be significantly altered by mechanically crimping the fibers. Furthermore, the mechanical bond is so strong that pull-out of the fiber is limited by the strength of the nylon fiber³³. This information has been determined for polymer composites that are not polymer concretes, however it is expected that similar features would be observed in PCTs.

The elastic modulus in fiber reinforced composites depends on beam dimensions, density and resonance frequency, and it can be affected by the presence of porosity and microstructural defects (voids or clusters)³⁴. Clearly then FRCs and likewise PCTs are structurally complex materials.

In the case of building structures, the non-destructive tests (NDTs) take into account the acoustic impedance of the system components - important factors influencing ultrasonic wave propagation. The dynamic elastic modulus is determined by measuring the pulse velocity along the composite and using electrical transducers located on the opposite sides of the cubic specimens of concrete. The energy supplied the ultrasound depends on how compact is the composite, including the void presence and sizes. One thus obtains the dynamic elastic modulus E_d :

$$E_d = V^2 \rho (1 + \nu)(1 - 2\nu)/(1 - \nu)$$

Here V is the pulse velocity; ρ is the mass density of the concrete specimen; and ν is the Poisson ratio. E_d necessarily depends on the component properties and their interactions with the matrix⁵⁵.

7. TESTING SPECIMENS

As the features of PCTs continue to be discovered and defined, standardized testing specimens are used for comparability. For compression tests cubic specimens (50x50x50 mm) are used (Figure 1), according to the [RILEM standard CPT PC-2 or ASTM C39-05 standard; the loading rate is 1.25 mm/min³⁵.

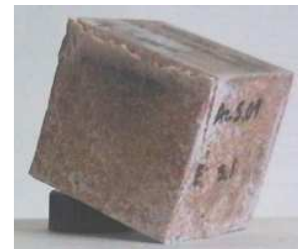


Figure 1. Cubic specimen of polymer concrete

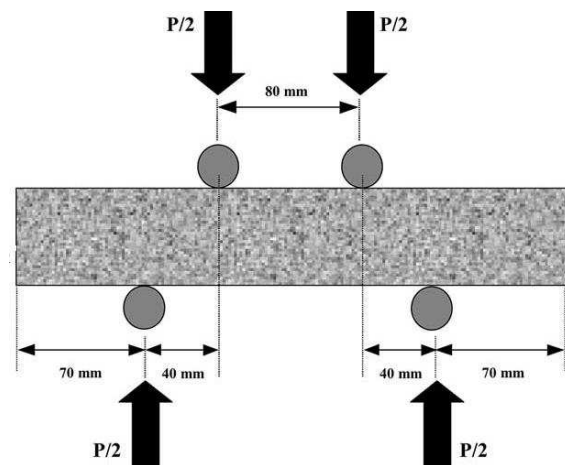


Figure 2. Four point bending test

For flexural and tensile strength tests prismatic specimens are used, with dimensions

40x40x160 mm or 70x70x 210 mm. Prismatic PCt beams with length span of 100 mm are tested in three or four-point bending up to failure at a loading rate of 1 mm/min²⁷ (Figure 2) (according to RILEM CPT PCM-8 standard or ASTM 293 standard^{36,37}).

8. GAMMA RADIATION

Improvements in PCts typically come from modifying the physicochemical properties of both the resins and the mineral aggregates. An alternative to modifications by thermal processes or chemical attack is to use gamma radiation, which may have more advantages than the previously named methods.

During the last five decades the applications in various fields where gamma radiation is used have been on the increase. It is well known that when using gamma radiation on polymers, three main processes occur: cross-linking, scission, and grafting of chains (which involves generation of free radicals). The likelihood of each process occurring depends on the specific polymer properties. Gamma radiation has proved its efficacy for improving the physicochemical properties of different kinds of polymers and for improving mechanical performance of building materials. The γ -rays have neither mass nor charge; and they are emitted from different sources, ¹³⁷Cs or ⁶⁰Co with 0.66 MeV and 1.33 MeV of energy, respectively^{38,39}.

Many advantages of gamma radiation over conventional curing processes are known⁴⁰⁻⁴⁴. a) It makes possible a complete and fast cure for certain polymers when the catalyst does not complete this work (and thereby permits addition of different additives or monomers). b) The chemical reaction can be started without a catalyst (therefore requiring no activation energy, only the energy of the radiation); the reaction is homogenous throughout the system, and the termination reaction is practically always diffusion controlled. c) Gamma irradiation can be performed at any temperature and be interrupted at a chosen reaction time. d)

The polymer can be analyzed at selected reaction stages. e) The process does not significantly increase temperature during reaction initialization compared with the highly exothermic behavior exhibited by non-irradiated processes. f) It results in better solvent resistance of the polymer and improved shape stability with respect to aging and to high temperatures. g) It allows tighter control of part dimensions and elimination of internal stresses which reduce material strength. h) There is no emission of volatile compounds to the environment.

The doses required for total cure strongly depend on the composition used, and it is necessary to evaluate the relationship between the curing and cross-linking processes, because sometimes they happen at the same time⁴⁰.

Gamma radiation produces a high rate of radical formation, orders of magnitude higher than with classical initiators. When using chemical initiators, the decrease of the overall activation energy (by a few kilocalories per mole) does not compensate for the increased radical concentration and poorer heat transfer. In radiation-initiated polymerization reactions, however, the overall activation energy may fall to very low values, making thermal explosions impossible⁴⁵.

Gamma radiation in polymeric resins and fibers: In the polyester resin mechanism, free radicals that are formed on the chains react with the double-bonds, releasing strain energy and resulting in polymerization. The 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 while scission of the chemical bonds increases. There is a dependence on the chain length, the strain and bond rupture; the shortest lengths have the highest strain energy, and they break first⁴⁶. The mechanism is complex, and a full illustrated narrative is beyond the scope of the present article.

When polymeric resins are irradiated chain

scissions also result in the formation of free radicals. Consequently, both radical and cationic cross-linking mechanisms can be occurring, for example in irradiated composites of epoxy resin and carbon or aromatic polyamide⁴¹. Moreover, the increase of chain scissions is assumed to cause an increase of mechanical creep deflection due to the breaking of the cage and the release of the local strain energy¹⁵.

In an *unsaturated polyester resin* submitted to gamma radiation, the reaction runs smoothly and the product is flawless as shown by the arrows in Figure 3b, contrary to badly foamed products from mixing with different catalysts, seen as “light” lines shown in Figure 3a (Ref.45). At the initial stage the polyester resin is in the form of viscous liquid, gelled material or glassy solid. At doses below 4 kGy a liquid state is maintained^{43,44}, and after this dose a measurable quantity of insoluble gel is formed (the boundary of the gelled region is indicated by a line in Figure 4a). The remaining liquid can be separated from the gel, after the microgel formation is completed (the microgel consists of spherical particles formed by an

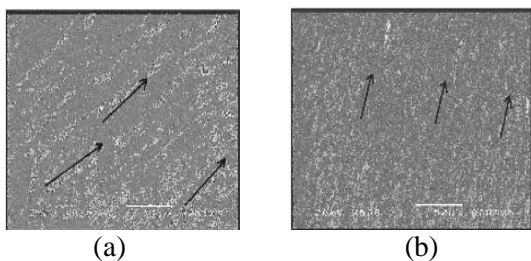


Figure 3. SEM micrographs of polymerized resin by using catalyst (a), or gamma radiation (b).

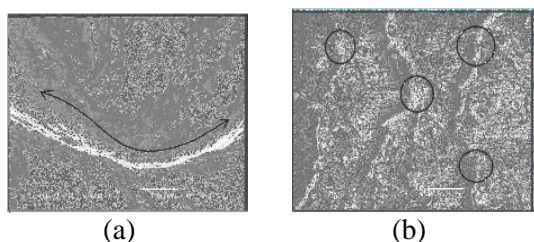


Figure 4. SEM micrographs of irradiated resin at 5 kGy (a) and at 10 kGy (b).

intramolecular crosslinking reaction between polyester insaturations and some styrene molecules located inside the polyester coil) Circles drawn on Figure 4b indicate the location of microgel particles. [A monotonic increase in the conversion percentage up to about 8 kGy occurs; at this stage a gel fraction and the styrene monomer are present. Multiple-phase products are formed in that stage of the reaction when the glass-rubber transition is below the reaction temperature (the curing temperature = 35°C). Afterward, vinyl monomers interconnect microgels to produce a three-dimensional network, and the resin system abruptly changes from a viscous liquid into a hard thermoset solid. Degradation of the polyester has been reported at a gamma dose of 50 kGy^{43,47}.

The radicals are at first formed in the molecular end groups, and after that scission occurs. When the chains with the radical are restrained by the surrounding chains, the radicals may rebind with the original chain (the recovery of the chain) before scission. The recovery of the chains due to restraints caused by the surrounding chains is called the “cage effects”. At low temperature when recovery occurs the total number of the scissions is believed to be proportional to the number of the radicals present. Due to the cage effects at high temperatures, the chains have “strain” energy caused by the initial “stress” of the surrounding chains. The radicals formed by gamma radiation are believed to help a given chain to escape from the restraint of the surrounding chains. The so-called cage breaks occur, with short chains breaking first¹⁵.

In the case of PET, different opinions about radiation stability have been reported. Some authors report fair stability in the physicochemical properties at high doses (900 kGy), with changes from cross-linking processes up to 35 % from the starting values. Similarly some have reported changes due to the chain scission process at low dose (from 0 to 10 kGy) while others have reported such events at high dose (from 120 kGy to 5 MGy). Radiation can cause both crosslinking and degradation (by chain scission). Whether both

of these processes occur in similar proportions – as in PET, located in the middle of the “pyramid” of Figure 5 – or whether one or the other dominates is dependent on the chemical composition of the polymer. In Figure 5, the further away a material is from the central axis, the more dominant is the corresponding mechanism. We also see a division of different polymers shown from the bottom to the top of the pyramid. The mechanism of the degradation for PET fibers or PET bulk is the same. No chemical degradation for PET fibers is found up to 200 kGy⁴⁸.

Gamma radiation in ceramic-polymer composites: Different mechanisms come into play when gamma radiation is applied on mineral aggregates. In calcium bentonite the effects of irradiation depend on the particle size distribution (clay and coarse), which in turn reflects differences in the mineralogical composition. For example, the thermoluminescence (TL) response of the coarse fraction in calcium bentonite is two orders of magnitude higher than the clay fraction, and the concentration of radiation-induced defects increased with increasing dose. Indeed, the coarse fraction has a higher concentration of defects (over one order of magnitude) than the clay fraction. These results are consistent with the fact that the coarse fraction contains minerals (silica and plagioclase groups) that are

very sensitive to radiation. In the case of the clay fraction, the gamma radiation promotes defects in its crystalline lattice, mainly affecting the stability of the Al-O and Si-O bonds. The defects are oxygen anion vacancies⁴⁹.

One of the most important applications of calcium bentonite is as an engineering barrier of long-lived radioactive waste materials from the nuclear industry, for example soluble salts, aqueous solutions (nitrates), oxides and glasses²⁵. The requirements for acting as engineering barrier consist in having radiation and thermal stability, leachability resistance and structural integrity. For example, aqueous nitrates with calcium aluminates, impregnated with styrene-divinyl benzene, have radiation stability to 100 MGy, which is the total integrated dose expected for 1000 years exposure²⁵.

Very little information concerning the effects of gamma radiation in composites of the type polymer matrix + mineral aggregates + polymeric fibers has been developed. Nevertheless, in the last decade studies on the effects in the bonding interaction at the interface, as well as modifications of the polymer phase and mineral aggregates (fillers) are of potential interest. Moreover areas involving predictions of the useful service lifetime in different service environments are also important to consider.

It is expected that the ionizing energy can improve compatibility between the aggregates and the polymer matrix by means of the structural and surface modification of both components. Thus improvement of the mechanical properties of PCt can be obtained.

For the composite polyester + styrene resin + gypsum, the gamma cross-links produced in the polymer chains reduce the mobility of the molecular segments (in the chains) in the vicinity of the filler particulates; thus the T_g increases⁵⁰. For low irradiation doses there is a slight increase of the T_g and then that temperature becomes constant. Due to the effective heat transfer, the inorganic filler

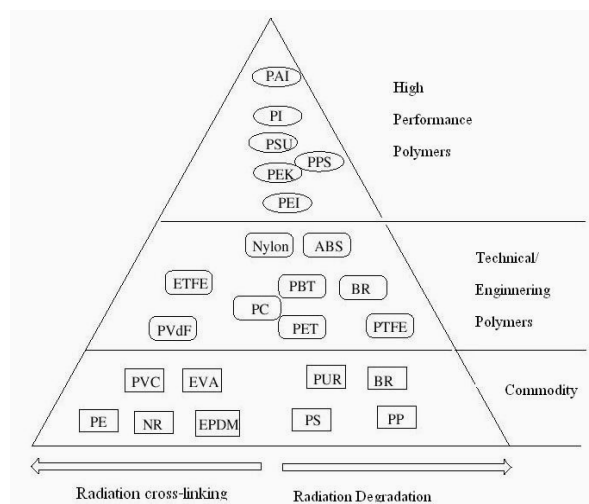


Figure 5. Effects of gamma irradiation on different polymers.

influences the thermal degradation of the polymer, in particular, the decomposition temperature goes down significantly⁵⁰. For this composite the compression strength and the tensile stress at break increase with increasing irradiation up to 320 kGy.

9. GAMMA RADIATION IN CONCRETE

The main interest of irradiated Portland cement concrete is focused on building construction at nuclear power plants (NPP), particle accelerators and irradiation buildings located in hospitals^{38,39}. Their deterioration limit for mechanical properties is higher than 100 MGy. Fortunately, the construction concrete of the nuclear power plants absorbs between 350 and 500 kGy of radiation dose when operating in normal conditions, during its service life (from 40 to 57 years)^{44,45}. PCC with added calcite (CaCO_3) shows a 10 % reduction in mechanical strength when subjected to 500 kGy of gamma radiation. Furthermore, crystallinity increases, with crystallites growing into the pores thus decreasing the porosity from 12 to 6 % (Ref.39).

Polymer concrete possesses sufficiently high strength and radiation stability. Additionally, it has low induced radioactivity, is not toxic and dusty, does not produce aerosols, and can be easily cleaned. The shielding properties of PCt can be varied over wide ranges so it can be employed favorably for the compact shielding of accelerators and other advanced technologies.

Studies by the authors concerning the effects of gamma radiation on polymer concrete show different behaviors based on the components (polymer resin and mineral aggregates)^{22,23,40,51-57}. Such studies are summarized in Figures 6 to 11. In Figure 6 is shown the compressive strength of PCts compounded with unsaturated polyester resin (UPR) and one or two mineral aggregates; also shown are values for specimens of 100% resin.

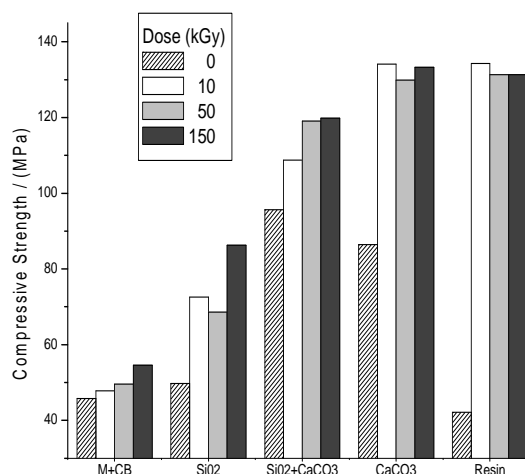


Figure 6. Compressive strength of polymer concrete compounded with different mineral aggregates. (M+CB = Marble + Calcium Bentonite)

In Figure 6 we see that the compressive strength values increase with the gamma irradiation dose. Moreover, when using CaCO_3 , the highest compressive strength values are obtained compared to using SiO_2 aggregates. Intermediate values are found when using a combination of them (CaCO_3 and SiO_2). For a combination of Marble and Calcium Bentonite (M+CB), very low values are obtained. The standard value of compressive strength for polyester-based PCts is 70 – 80 MPa²³. Thus, for 100% of resin the values are comparable with those for PCt with CaCO_3 . Such resin could be used for certain applications. However it has a high cost. Fortunately in the PCts shown it represents only 30 wt. %.

With respect to fiber-reinforced PCts, Figure 7 shows that the compressive strength values increase when the gamma irradiation dose increases. Different types of fibers were used (Nylon=N, Polypropylene=PP, and Polyester=P) at varying percentages (0.3, 0.4 and 0.5 vol. %) and with similar dimensions (40-60 μm of diameter and 10-20 mm long). The lowest values of compressive strength were

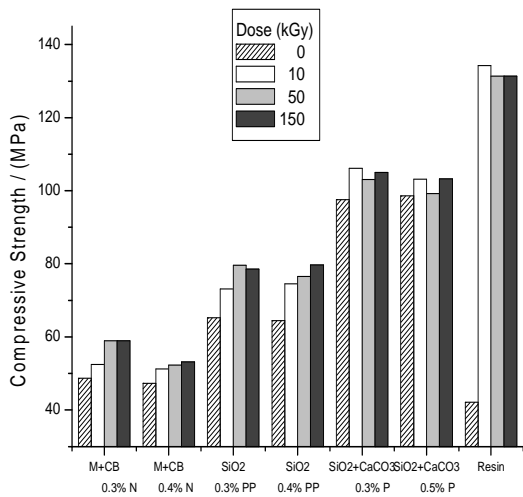


Figure 7. Compressive strength of fiber-reinforced polymer concrete compounded with different mineral aggregates. Abbreviations: Marble + Calcium Bentonite (M+CB); Nylon (N); Polypropylene (PP); Polyester (P).

observed for PCt with Marble + Calcium Bentonite, independently of the Nylon-fiber percentage. The Nylon fibers have a rigid shape, which differs from the polypropylene or polyester fibers having a more elastic shape. Thus the compressive strength depends on the material type, that is to say either rigid or elastic. In our studies the highest values have been found in formulations combining two mineral aggregates (CaCO₃ and SiO₂). Not all combinations of resin + aggregate + fiber have been tested yet as work in this area is ongoing.

Another important mechanical feature of the PCts is related to the compressive strain at the yield point, as seen in Figure 8. The highest compressive strain values are for PCt with Marble and Calcium Bentonite (M+CB); that is followed by PCt with CaCO₃. These results are higher with respect to the standard values reported in the literature (0.01 mm/mm)⁴⁰. On the other hand, lower values are observed for PCt containing SiO₂ or CaCO₃+SiO₂. In general the values increase up to a certain dose and afterward decrease for higher doses. In the case of PCt with CaCO₃ the maximum value is obtained at 10 kGy; the same behavior occurs for PC with SiO₂ and for 100% resin. One

conclusion is that when using one mineral aggregate the compressive strain is influenced more by the resin than by the mineral aggregates.

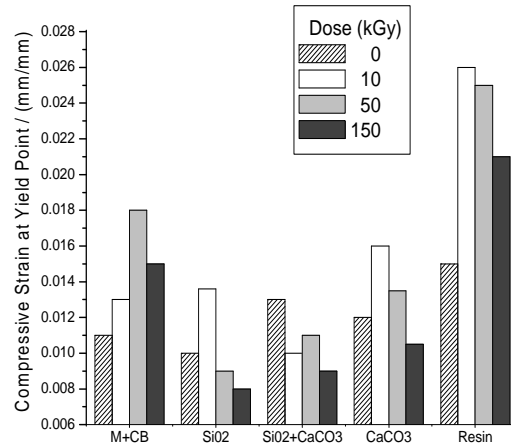


Figure 8. Compressive strain at yield point of polymer concrete compounded with different mineral aggregates. (M+CB = Marble + Calcium Bentonite)

In the case of fiber-reinforced PCts, the compressive strain values increase notably for materials with two mineral aggregates (CaCO₃ and SiO₂) rather than just one (SiO₂) (Figure 9). Something notable is that when comparing these compressive strain values to the standard value reported in the literature for PCt (0.01 mm/mm)⁴⁰: a) for PCt with SiO₂ there is 60 % improvement; b) for PCt with M+CB up to 180 %, and c) for PCt with CaCO₃ and SiO₂ up to 390 %. So, it is worth point out that the combination of two minerals and elastic fibers (polyester and polypropylene) and at least 10 kGy of gamma irradiation allows higher values of compressive strain.

A third mechanical feature studied was the Young's modulus. Excepting only PCt with M+CB, the values are higher (see Figure 10) than the standard value for polyester-based PCts, namely 6.7 GPa¹⁷. Moreover, the improvement above that standard is notable: a) 143 % for PCt with SiO₂, b) 141 % for PCt with CaCO₃SiO₂, and c) 120 % for PCt with CaCO₃+SiO₂. Generally the higher the gamma

irradiation the higher the Young's modulus and the harder the PCt becomes.

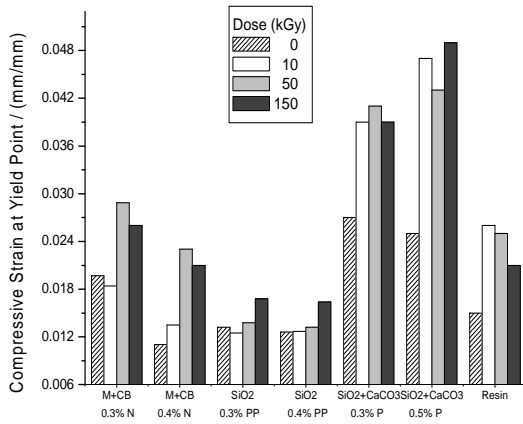


Figure 9. Compressive strain at yield point of fiber-reinforced polymer concrete compounded with different mineral aggregates. Marble + Calcium Bentonite (M+CB)

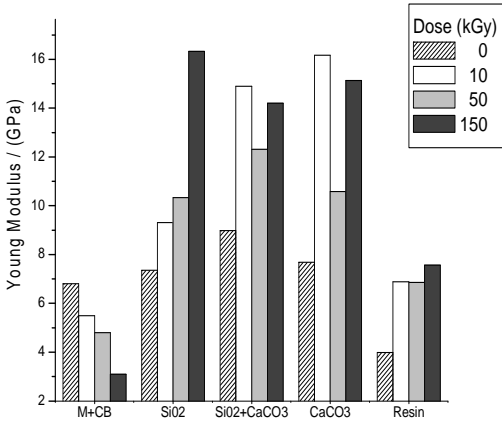


Figure 10. Young's Modulus of polymer concrete elaborated with different mineral aggregates

In the case of fiber-reinforced PCts, the behavior of the Young's modulus is significantly varied (Figure 11). The PCt with SiO₂ has higher values with respect to the standard reported for polyester-based PCts (6.7 GPa)¹⁷. Nevertheless, it is possible to obtain low values for PCt with CaCO₃+SiO₂, namely 2.8 GPa, which represents a diminution of 58 % with respect to the standard. It is therefore also possible to get a more ductile PCt, which may

be desirable for certain applications. For PCt containing M+CB or SiO₂ an irradiation dose of 10 kGy appears to result in the maximum value of the modulus. By contrast, for the PCt with combined SiO₂ and CaCO₃ the irradiation has little effect, likely due to competing interactions and effects in these materials.

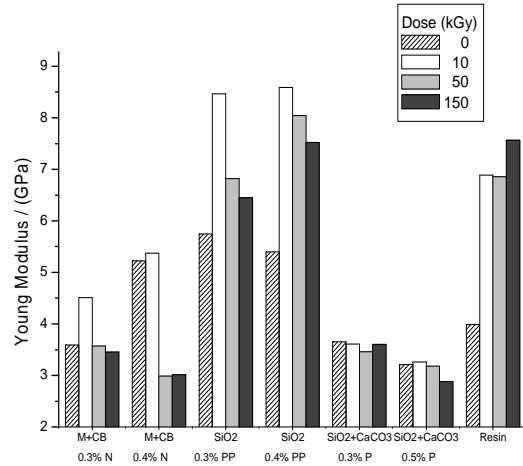


Figure 11. Young's Modulus of fiber-reinforced polymer concrete compounded with different mineral aggregates

The Young's modulus E is proportional to the storage modulus E' obtained by dynamic mechanical testing (DMA), except at very large deformations⁵⁸ (we are the only ones who studied this). In turn, E' is inversely proportional to brittleness⁵⁹⁻⁶¹. Therefore, improvements of E described here have wider implications and may be indicative of improvements or modifications to other properties not directly tested. It is therefore evident that the use of gamma irradiation can be another strategic tool to modify the mechanical properties of polymer concretes.

BRIEF CONCLUSIONS

The objective of this report has been to describe the special characteristics of polymer concretes (PCt) as well as the role of how additives and processing can enhance PCt properties. In that regard we have discussed fiber reinforcement of PCts, and especially the effects of gamma

irradiation on the curing process. It has been shown that combining fiber reinforcements and the matrix curing effects of irradiation can provide significant improvements to the properties of PCt.

It is hoped that further studies into developments of PCt properties and applications may find this overview a useful resource.

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