Gamma Radiation as a Novel Technology for Development of New Generation Concrete

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1. Introduction

Global development demand new technological creations at less costs. Inside the specialized industry, composite materials usage is well known. That is why it is of major importance research and development of new composite materials for technological applications, as in the construction industry.

The composite materials usage has increased rapidly during the last few decades in building construction; showing different properties as reduction in weight, reduction on the fatigue and corrosion. As we know, a key issue with composite technology is that the final characteristics of a material are established at the time of fabrication of the goods. Therefore, part design, fabrication development and material characterization must proceed concurrently.

The production of polymer concrete can be developed for semi-industrial and industrial scales for its economical advantages, as well as environmental benefits if its main raw materials are wastes. In such composite materials the polymeric materials are able to compete and contribute substantially to the development of better, cheaper and more functional products.

In polymer concrete some engineering polymers are widely used due to their excellent mechanical, thermal and chemical properties. These properties are direct consequence of their composition as well as their molecular structure. Nowadays, mechanical properties of polymeric materials are of great interest and can be improved by composition and/or morphological modifications, in order to change the softening temperature and get their elastic solid state back [Menchaca et al., 2011].
The developments in the study and applications of radiation effects have been rapidly increasing research activity towards the development and understanding of novel synthetic materials with particular emphasis on their properties, synthesize, analyze and modify such new materials.

Radiation chemistry is defined as the study of chemical effects caused by the passage of ionizing radiation through matter. Ionizing radiation comes from substances undergoing nuclear transformations, from outer space in the form of cosmic rays and from particles accelerators. It includes $\alpha$, $\beta$, and $\gamma$ rays from radioactive nuclei, charged particles such as protons and deuterons and X-rays of wavelength less than approximately 250 Å [Wilson, 1974].

Each particle of ray of ionizing radiation produces a large number of ionized and excited molecules along its track. The ionizing radiation is no selective and may interact with any molecule in its path and raise it to any of its possible ionized and/or excited states (Figure 1). The heterogeneity of the latter type of reaction is especially marked in the liquid and solid state [Wilson, 1974].

Fig. 1. Effects produced by radiation throughout matter.

There are two main types of radiation sources: a) radio isotopes, and b) devices such as X-rays tubes and electron accelerators. The isotope most frequently used as radiation source is $^{60}$Co, mainly because of its advantageous properties: availability, high energy gamma-rays, 5.3-year half live [Wilson, 1974].

Once that high energy or ionizing radiation penetrates into the matter, its energy is lost due to the interaction with the molecular valence orbital electrons that are found on its path. As a result, these electrons are promoted to higher levels of energy (excitation) or pulled out from their orbital (ionization). The basic chemical transformations that happen in a molecule subject to irradiations can be summarized as follow in Figure 2 [Mykiake, 1960]:

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Ionizing radiation can be used for understanding mechanism of polymerization reaction as well as for initiation of the polymerization process. Some of the advantages of the radiation initiated polymerization over the conventional methods are: a) Curing at ambient temperature; b) absence of foreign matter, like initiator, catalyst, additives; c) polymerization at low temperature, or in solid state, d) rate of the initiation step can easily be controlled by varying dose rate, e) better solvent resistance of the polymer and its improved shape stability with respect to aging and to high temperatures [Chapiro, 2002]; f) better control of part dimensions and elimination of internal stresses which reduce material strength; shorter curing times; and no emission of volatiles to the environment.

The radiation chemistry of polymers provides a research field that is full of fresh and stimulating discoveries. Polymers are most sensitive to slight variations of the chemical bond, in this way, initial features and properties may be varied and new materials may eventually be tailored [Charlesby, 1952; Dole, 1950].

When polymers are irradiated their extremely long molecular chains can be broken easily by the absorption of a quantum of energy above the energy of the covalent bond of the main carbon chain, which typically is in the range of 5 – 10 eV. The energy of gamma photons of some MeV surpasses by many orders of magnitude this minimum value, representing a high risk of degradation to all kind of polymers, naturals and synthetics alike. However, by controlling the applied doses, degradation of polymers of large molecular mass – or even of cross-linked molecular structures – has been a field of radiation application.

As it is known one of the main effects of the ionizing radiation over polymeric materials is the formation of cross-linked molecular structures, and the degree of the cross-linked effect depends on the applied doses. In polymer chemistry, when a synthetic polymer is said to be "cross-linked", it usually means that the entire bulk of the polymer has been exposed to the cross-linking method. The resulting modification of mechanical properties depends strongly on the cross-link density. Low cross-link densities raise the viscosities of polymer melts. Intermediate cross-link densities transform gummy polymers into materials that have elastomeric properties and potentially high strengths. Very high cross-link densities can cause materials to become very rigid or glassy.
Cross-links can be formed by chemical reactions that are initiated by heat, pressure, change in pH, or radiation. For example, mixing of a unpolymerized or partially polymerized resin with specific chemicals called crosslinking reagents results in a chemical reaction that forms cross-links. Cross-linking can also be induced in materials that are normally thermoplastic through exposure to a radiation source, such as electron beam, gamma radiation, or UV light.

Cross-links are the characteristic property of thermosetting plastic materials. In most cases, them is irreversible, and the resulting thermosetting material will degrade or burn if heated, without melting. Especially in the case of commercially used plastics, once a substance is cross-linked, the product is very hard or impossible to recycle. In some cases, though, if the cross-link bonds are sufficiently different, chemically, from the bonds forming the polymers, the process can be reversed.

Another result of polymers irradiation is that smaller hydrocarbon chains will be formed (lighter hydrocarbons and gases) as well as heavier hydrocarbons by recombination of broken chains into larger ones. This recombination of broken hydrocarbon chains into longer ones is called polymerization. Polymerization is one of the chemical reactions that takes place in organic compounds during irradiation and is responsible for changes in the properties of this material. Some other chemical reactions in organic compounds that can be caused by radiation are oxidation, halogenation, and changes in isomerism.

The polymerization mechanism is used in some industrial applications to change the character of plastics after they are in place; for example, wood is impregnated with a light plastic and then cross-bonded (polymerized) by irradiating it to make it more sturdy. This change in properties, whether it be a lubricant, electrical insulation, or gaskets, is of concern when choosing materials for use near nuclear reactors.

When the geometry of the bond structure is modified using gamma-irradiation, the characteristics of the long chains of polymers vary, thus some changes in polymer properties can be explained through induced chain strength, chain re-orientation and crystallinity. On the other hand, depending on the dose cross-linking or chain scissions may be present in irradiated polymers.

It has been claimed that chain scission occurs either in the amorphous region [Pattel & Keller, 1975; Jenkins & Keller, 1975; Ungar & Keller, 1980] or inside the crystals [Hoseman et al., 1972; Loboda-Cackovic et al., 1974]. Also it was reported that both process begin with the formation of free radicals [Timus et al., 2000; Valenza et al., 1999; Bittner et al., 1999] followed by the Compton Effect [Bittner et al., 1999; Yu & Li, 1998]. Some researchers establish that the main process in polymers, due to high radiation energy, is that of cross-linking [Balabanovich et al., 1999; Charlesby, 1960]. Others propose the chain scission as the main effect [Timus et al., 2000; Bittner et al., 1999] and even some others show that both processes can happen [Timus et al., 2000; Valenza et al., 1999; Balabanovich et al., 1999; Charlesby, 1960; Barkhudaryan, 2000a; Barkhudaryan, 2000b; Delley et al., 1957; Gupta & Deshmukh, 1983; Li & Zhang, 1997; Zhang et al., 2000] all of them as a function of the experimental conditions and the type of polymer under study. Also it was reported that both processes begin with the formation of free radicals [Timus et al., 2000; Valenza et al., 1999; Bittner et al., 1999].
A mechanism for chain scission occurring in the amorphous zone of the nylon 6,12 at high radiation dose which takes into account the Compton Effect has been proposed [Menchaca et al., 2003]. In the same work, cross-link is under consideration in the low dose region. An study of the low gamma irradiation dose (up to 50 kGy) has shown that the cross-link process is taking place in the amorphous zone of the nylon 6,12 [Menchaca et al., 2003; Menchaca et al., 2008]. When gamma radiation at low dose is applied both, the fusion temperature and the crystallinity degree show evidence of increments [Thanki et al., 2001], as well as a partial and repairable damage in the amorphous zone, is reported [Malek et al., 2001]. The last phenomenon produces the so called re-polymerization process involving chain reorganization.

2. Effects of gamma radiation on components of concrete

2.1 Polymeric materials: Resin and fibers

The unsaturated polyester resins (UP) are most widely used thermosetting resins and are being increasingly applied for various purposes because of their easy handling, balanced mechanical and chemical characteristics and a cheap price.

The cross-linking reaction of UP resins is usually initiated by a thermal or redox initiator. The cross-linking reaction occurs by heterogeneous free radical mechanism and it follows different periods: a) The induction period during which there is no cross-linking until the inhibitor is used up; b) The propagation period: the reaction starts and its rate depends on the mass law. As the 3-D network appears, it reduces the availability of reactants; diffusion-controlled part of propagation period begins. When, because of restrictions imposed by the network, termination of macro-radicals ceases, the reaction rate significantly increases and so called “gel effect” occurs; c) In the final reaction period, vitrification of the system takes place and the cross-linking stops; the propagation period of the cross-linking reaction should be distinguished from the free radical reaction step of the same name.

The micro-gels are caused by intra-molecular reaction between polyester insaturations and some styrene molecules present inside the polyester coil because the concentration of styrene inside the coil is lower [Jurkin & Pucic, 2006]. Further in the reaction, vinyl monomers interconnect micro-gels to produce a 3-D network, and the resin system abruptly changes from a viscous liquid into a hard thermo-set solid. Still, a part of un-reacted polyester double bonds remain mostly buried inside micro-gels.

As we know the effects of the passage of electromagnetic radiations through matter produces three main type processes: a) Photoelectric effect, b) Scattering of free electrons as Thompson, Rayleigh and Compton Effect, and c) Electron-positron pair production [Menchaca et al., 2011]. These effects are permitted by the energy range that the particle or photon radiation can give to the molecules, atoms or ions in the matter structure. However in gamma irradiated polymeric materials, for instance, the Compton Effect is the most important due to the energy of the gamma photons (1.17 MeV and 1.33 MeV) and the low density of the polymers.

The effects of ionizing radiation in polymers depend on the structure and density of each polymer. These effects can be: cross-link of the molecular chain of the polymer, damage in
crystalline regions, degradation of the polymer, and the possibility of the molecular weight changes of some polymers for changing physical and chemical properties [Martinez-Barrera et al., 2004].

The alternative route of curing UP resins is radiation processing that has many advantages over the conventional methods: no catalyst or additives are needed to initiate the reaction and it can be performed at low temperatures. The initiation is homogeneous throughout the system and the rate of cross-linking is easily controlled by varying the dose rate.

Curing polyester resins involves chain scissions which result in the formation of free radicals. The radicals react with the double-bonds and release strain energy resulting in polymerization. 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 is done; the shortest chains have the highest strain energy and they break first [Nishiura et al., 1999].

By contrast, in gamma irradiated resins the reaction runs smoothly and the product is flawless - unlike badly foamed products obtained when using catalysts. As we know thermoset resin containing double bonds (C=\(\text{C}\)) in the presence of a monomer, when exposed to a limited dose, will partially cross-link to form a stable 3-D gel. As a result, the mixture is no longer a viscous liquid. Instead, it becomes a viscoelastic gel. When irradiation impacts resin that contains an initiator, active species are created along the path of the incident electrons. These active species then react to create cross-links in the material. As a result, clusters of cross-linked material have formed, giving structure to the material. This in turn, restricts the movement of the large polyester oligomers and the material develops viscoelastic properties.

Polyester isophthalic resins dissolved in 36\% by weight styrene were irradiated at six different doses (from 5.5 to 33.3 kGy) with a ratio dose of 4.1 kGy [Woods & Pikaev, 1994]. Several results were found. By measuring the deformation due to a compressive load on the sample resin, a relationship was developed between the compressive load and the degree of cross-linking. The maximum compressive loads for sample resins without initiator varying from 20 to 200 N, these values are lower than those for sample resins with initiator (from 30 to 320 N), which means a maximum difference of 116\% [Czayka et al., 2007]. This would indicate that under irradiation, some of the initiator is contributing to cross-linking.

More interesting is the comparison between modifications with irradiation vs with chemicals. The values for irradiated resins show 151 MPa as maximum tensile, 10.9 GPa for tensile modulus and 1.8\% of the strain at break. These values are 18, 14 and 20\% bigger, respectively, than those for modified resins by chemicals [Czayka et al., 2007]. Moreover, for the total enthalpy, which is represented by the area under the heat flow vs. time curve; The enthalpy transitions became broader as the cross-links form with dose increase, there is less mobility and hence, the rate of cross-linking decrease. The enthalpy change, decrease from 242 to 185 (J/g) and the fraction cross-linked increase from 0.19 to 0.38 when increase the irradiation dose.

The degree of polymerization can be follow by selected wavelengths. The wavelengths for styrene monomer and for polystyrene that may be polymerized during irradiation include
the carbon–carbon double bonds at 982 cm\(^{-1}\). If radiation is cross-linking the material, then the magnitude of this peak should decrease with increasing dose levels. When the dose increases the peak height for the styrene decreases, in the region where the polystyrene peak should occur, there is none. This means that there is no measurable indication that homopolymerization of the styrene is occurring during irradiation.

A total and fast cure for certain polymers is achieved by gamma radiation in the cases when the catalyst does not complete its function, as total polymerization process of the polymer resin [Delahaye et al., 1998; Martínez-Barrera et al., 2006]. This eliminates the need for further 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 required doses for total cure strongly depend on the composition used; it is necessary to evaluate the rate of cure progress.

During UP resin cross-linking, full conversion is never reached. Post irradiation reaction polymerization continues after the irradiation was ended due to free radicals formed trapped and stabilized in macromolecules or in the network. In gamma irradiated UP resins (from 1 to 6 kGy at dose rate of 39.13 kGy/h), depending on the dose at which the irradiation was terminated, the samples are in form of viscous liquid, gelled material or, at the highest dose, glassy solid. At doses below 3.5 kGy the samples remained liquid, while those irradiated to higher doses formed measurable quantity of insoluble gel.

The extraction analysis offers the possibility to analyze the post-irradiation changes of the free styrene content, separately of those of the gel content. During the 15 days post-irradiation period monitoring, the gel content increased while the corresponding free styrene content decreased [Jurkin & Pucic, 2006]. Sharp rise in viscosity at 4 kGy, caused by the more dense network formed during irradiation, greatly reduced the post-irradiation cross-linking.

The extent of post-reaction increased again as the irradiation was terminated in the gel-effect dose range, 4.5 to 5 kGy. At the highest dose, 6 kGy, radiation reaction approached maximum conversion and the system vitrified, thus impeding the post-effect at room temperature, so the fraction of post-irradiation formed gel decreased again.

Still the shape of DSC traces and corresponding heats of the residual reaction offer plenty information on the post-irradiation cross-linking. At all doses above the induction period threshold (3 kGy), on the day of the irradiation, two exothermic processes were seen [Jurkin & Pucic, 2006]. The lower temperature process had a maximum at about 120°C and the broad higher temperature exotherm had a maximum between 160 and 200°C. The lower temperature process was attributed to both the styrene-polyester copolymerization and the styrene homopolymerization.

In the case of polymeric fibers, the re-polymerization and reorientation processes are favoured when they are irradiated, producing longer but oriented chains, compared to the original ones. The scission chain mechanism produced by gamma irradiation, primordially located in the amorphous zone of the fiber, is not enough to break down the carbon-heteroatom or carbon-carbon bonds continuously and produce free radicals. In fact, the few free radicals produced react immediately to form long chains. Nevertheless, such kind of energy is not enough to break the bonds repeatedly and produce smaller species, as it
happens in irradiated-fiber at higher dose [Menchaca et al., 2009]. Such mechanism predicts an increase in the fusion temperature, as well as in its crystallinity, since the chains are broken down in the amorphous zone and reoriented, yielding new crystalline zones [Menchaca et al., 2011].

The structural changes caused on irradiated-nylon fibers are reflected in their morphology. It can be observed different kind of modifications on the surface depending on the radiation dose applied. Figure 3a shows the morphology of the non-irradiated nylon fiber, which includes a surface with protuberances, strips and scratches. When the radiation dose increases to 5 kGy small particles are scrapped of these protuberances and better strips definitions are noticed. For higher irradiation dose more roughness and scratches are formed (Figures 3b), therefore superficial defects and scratches are more evident, as the dose is augmented (Figure 3c).

The damages can be related to crystallinity changes, because the formation of oligomers during gamma irradiation exposure provokes changes in the density, visco-elasticity, rheological and mechanical properties [Menchaca et al., 2011]. At the same time, these “damages” due to the radiation exposure increase the surface roughness [Menchaca et al., 2010] helping to grip some other kind of materials to the polymer in order to get materials with enhanced properties, e.g. concrete.

A post-irradiation study on nylon fibers show changes in the morphology with time. For the freshly irradiated fibers, mean crystal size tends to diminish (Figure 4a) probably because chain scission is generating more crystalline areas but with less size. Almost the same behavior is observed in the 3 years irradiated fibers, where mean crystal size tends to diminish from 15 to 50 kGy. Above 100 kGy there are not observed changes. The differences between freshly irradiated and 3 years irradiated fibers are the crystallites sizes. With time, crystal size increase meaning that whatever the reaction mechanism is taking place, after three years generation of new crystalline areas still goes on (Figure 4b).
On the other hand, the melting point has a general trend to decrease with no significant differences in temperature, just a slight increase as a function of time for the 3 years irradiated condition (Figure 5). But, the peculiar low dose response can be observed again. At 15 kGy and 50 kGy the melting point for gamma irradiated fibers is above or at least at the same temperature compared to the non-irradiated fibers. This phenomenon is attributed to the cross-link or partial damage [Wilson, 1974; Menchaca et al., 2003], and the decrease in the fusion temperature is ascribed to the chain scission or permanent damage that yields oligomers [Ramesh, 1999].

Fig. 5. Post-irradiation behavior of melting point.

Gamma irradiation causes both immediate and time dependent changes in the mechanical properties and there is considerable experimental evidence that the time dependent effects arise from the presence of long lived free radicals. Chain scission processes occur both during and after irradiation, leading to release of inter-lamella tie chain material which then
causes an increase in crystallinity. Mechanical changes can be closely related to the crystallinity increase and are of considerable importance in property critical applications.

Research concerning to the micro-mechanical deformation mechanisms of irradiated and non-irradiated isotactic polypropylene (iPP), studied as a function of temperature above the glass transition has been reported [Zhang & Cameron, 1999]. Several deformation mechanisms were identified and included lamellar separation, shear, stable and unstable fibrillated deformation and cavitation. The ductile–brittle transition rises dramatically with irradiation, while the glass transition shows only a small increase. This observation is explained by irradiation, through chain scission and cross-linking, having a dominant effect on large-scale plastic deformation and a lesser effect on the deformation which relies on the amorphous phase alone [Zhang & Cameron, 1999].

Polypropylene is an important structural material. In some circumstances, for example during sterilization for medical applications, it is subjected to significant doses of gamma irradiation, inducing significant change in mechanical properties. The response of the semi-crystalline structure to mechanical stress, before and after irradiation, is therefore of considerable interest. Isotactic polypropylene is a semi-crystalline polymer, which may crystallize into one of the three isomorphs, termed α, β and γ [Varga, 1995]. Conventional thermal processes result in spherulites with crystals of the monoclinic α isomorph [Varga, 1995]. All such spherulites possess radial lamellae, but under certain crystallization conditions, tangential lamellae may also be present [Padden, 1995; Norton & Keller, 1985; Lotz & Wittman, 1986; Olley & Basset, 1989; Padden & Keith, 1959; Idrissi et al., 1985]. It is reported that most bulk crystallised samples contain spherulites of mixed character [Norton & Keller, 1985] in which some areas of the spherulite are richer in tangential lamellae than others [Padden & Keith, 1959]. A range of spherulite types will be present if the crystallization temperature is not constant.

Polypropylene subjected to gamma irradiation undergoes cross-linking and scission [Nishimoto & Kagiya, 1992; Carlsson & Chmela, 1990]. In the presence of air, oxidation will enhance these effects [Carlsson et al., 1985]. Post irradiation ageing may occur as free radicals formed during irradiation react after the irradiation has ceased [Carlsson & Chmela, 1990; Carlsson et al., 1985]. Studies on isotactic polypropylene indicate that irradiation at 50 kGy in air causes slight increment of the crystallinity and the glass transition temperature to rise by a few degrees [Zhang & Cameron, 1999]. The changes to the dimensions of the lamellar architecture are small. It is widely reported however, that radiation does introduce major deterioration in mechanical properties of polypropylene as a consequence of chain scission and cross-linking [Kagiya et al., 1985; Nishimoto et al., 1991; Rolando, 1993; Martakis et al., 1994; Nishimoto et al., 1986; Kholyou & Katbab, 1993].

2.2 Mineral aggregates

Different mechanisms come into play when gamma radiation is applied on mineral aggregates. A few studies have been carried out. Some results have been reported for calcium bentonite which consists of a coarse fraction and a clay fraction. The concentration of radiation-induced defects increases with increasing dose. The coarse fraction has a higher concentration of defects (more than one order of magnitude) than the clay fraction. These results are consistent with the fact 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 holes trapped in the former positions of O atoms in the structure [Dies et al., 1999].

One of the most important applications of calcium bentonite is as engineering barrier for long-living radioactive waste materials from the nuclear industry such as soluble salts, aqueous solutions of nitrates, oxides and glasses. The requirements for acting as an engineering barrier include radiation and thermal stability - and also structural integrity.

### 3. Polymer matrix + polymeric fibers + mineral aggregates:

**Effects of gamma radiation**

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.

Hydraulic concrete surface coated with a solution of polymethyl methacrylate, loading from 4.7 to 5.1 wt%. The methyl methacrylate (MMA) forms a hard glassy polymer, strongly bonded to the cement matrix, which substantially improves the properties of the original concrete [Levitt et al., 1973]. The presence of moisture can reduced the polymer loadings; the initial surface absorption results reached their best values when water is present in the concrete at the time of impregnation. The values in excess indicate that in polymer concrete composites, the strength of the impregnated concrete matrix may exceed that of the added flint gravel aggregate (gravel+sand). The fracture occurs through shear failure of the aggregate, and this behavior is typical for all the impregnated samples.

Hydraulic concretes were soaked in the unsaturated polyester resin at different impregnation times ranged from 1 to 15 hours. The addition of polymer to the hardened concrete causes healing of micro-fractures and produces improved bonding between the cement paste and aggregate [Ismail et al., 1998]. The main factor which influences the unsaturated liquid absorption is the accessibility (i.e., permeability) of polyester to the pores of the samples. The degree of polymer impregnation increases with the increase in impregnation time reaching a saturation state at 5 hours, after which the degree of impregnation is relatively constant up to 15 hours. So, the degree of incorporation is namely dependent upon the amount of monomer introduced into the porous samples.

The final strength of the composite is dependent on a number of factors: namely the extent of the impregnation and filling of pores, the type and content of resin, the size of aggregate. The type of polymer and its ability to carry stress the degree of conversion of monomers to polymer during the polymerization, the formation of a continuous polymer phase and the mechanical properties of polymer.

The mechanical properties for polyester-filler composites depended on the type and amount of filler and also on the particle size of the filler used. Nevertheless, high filler content is important from an economical point of view and if this is a recycled material comes from
waste materials, as recycled PET form soft drink bottles and marble waste materials, the PC has acceptable physical properties, good mechanical integrity, enhanced chemical characterization, and providing better heat and flame resistance [Tawfik & Eskander, 2006].

In the case of polymer concrete, the physical and mechanical properties of cross-linked polyesters depend mainly on the type and ratio of the copolymerizable monomer used, for example of the styrene content.

Different concentrations for PC are suggested: for example 88 % of minerals and 12 % of styrenated polyester resin (SP); the minerals include 30% basalt (diameters: 0.5-1.0 cm), 40% marble (0.1 - 0.5 cm), and 30% marble (> 0.5 cm). It is recommended to dried the filler at elevated temperatures (for example at 273°C). For these PCs the compressive strength values increase as the styrene content increase, until a maximum of 123 MPa, at a polyester/styrene ratio of 60:40 wt %. Moreover, lower percentages of basalt reduce 36 % the compressive strength. Other studied on hydraulic concrete whose surface was coated with a solution of polymethyl methacrylate, the compressive strength increases according to the aging, after one day is 45 MPa and at 28 days 60 MPa.

Physicochemical modifications by using chemical attack or thermal processes are consuming time and money. An alternative for the preparation of composites is to use ionizing energy; the high energy radiation has special advantages, for example the controlled polymerization can be initiated uniformly within substantial thicknesses of material. Moreover, it is possible to improve compatibility between polymer matrix and the mineral aggregates - by means of structural and surface modification of both resin and the aggregates. Thus improvement of the mechanical properties of polymer concrete can be obtained.

Some results have been reported on formation of chemical links between aggregate minerals and polymer chains. For example, in silica + polysiloxane-rubber composites the induced cross-linking enhances crystallization rates and thus enhances mechanical properties at high strains. At the same time, a reduction in polymer-filler interactions at interfaces in silica + siloxanes composites is seen; the silica is modified by irradiation and a high surface area is obtained. Gamma radiation excites electrons sufficiently so that they leave their normal positions (valence to conduction band) producing positive holes and free electrons. Positive holes are electronic defects in the silica O$_2^-$ matrix created as a result of removal of an electron from the O$_2^-$ sites, which then become O$^-$ sites [Patel et al., 2006].

Mortar with impregnated polymer was subject to gamma irradiation for polymerization. The impregnated samples were subjected to 50 kGy with a dose rate of 10 kGy/h. The physico-mechanical properties were studied. The results show that the polymer loading, compressive strength, and bulk density increase with the increase in the percentage of cross-linking agent as well as the gamma irradiation doses [Ismail et al., 1998]. This behavior is attributed to the amount of polymer deposited in the pores of the specimens.

For a given gamma irradiation dose, the degree of polymer impregnation of the hardened cement mortar samples increases with the increase of the immersion time in the unsaturated polyester resin up to 4-5 hours. Moreover, the compressive strength also increases with the increasing impregnation up to 4 hours reaching an improvement of 59% when comparing to non-irradiated sample. This is attributed to the interaction between calcium silicate hydrates
and polyester formed in the pores of the hardened mortar during the polymerization process under the effect of gamma irradiation. A continuous polymer phase is formed within the cement matrix inhibiting the formation and propagation of microcracks in the matrix when the cement gels shrink upon drying.

The gamma radiation polymerization of hydraulic concretes impregnated with methyl methacrylate show substantial improvements: 208% for the compressive strength (respect to non-irradiated concrete =35 MPa), 247 % for the bending strength (non-irradiated =4.4 MPa), and 46% for the dynamic modulus of elasticity (non-irradiated = 27.7 GPa); such elasticity improvements are not sufficiently high to indicate the development of brittleness. The concrete samples were irradiated with gamma radiation from a $^{60}$Cobalt source, at 35 kGy with a dose rate of 0.75 kGy/h [Levitt et al., 1973].

The influence of irradiation dose on the thermal degradation reaction of polyester–styrene resin and polyester-styrene resin/gypsum composites in presence of nitrogen has been investigated. The composites were irradiated at ambient temperature and a dose rate of 6.0 kGy/h. The decomposition temperatures for both systems are determined for irradiation doses ranged between 10 and 320 kGy [Ajji, 2005]. Dose at 20 kGy is more than enough to harden the composites. The TMA thermograms with alternated force show significant increase on the elongation at the glass transition temperature. The $T_g$ for polyester-styrene resin vary from 67 to 78°C, and for polyester-styrene/gypsum from 77 to 86°C, when irradiating from 20 to 320 kGy. This means a 14% of difference when gypsum is aggregated. In both cases, there is a slight increase of the glass transition temperature for low irradiation doses and then the temperature becomes constant. This can be explained that cross-links built between the polymer chains via irradiation reduce the segmental mobility of the chains.

Moreover, the $T_g$ of the polyester-styrene resin/gypsum composites is higher than the glass transition temperature of polyester-styrene resin irradiated at the same dose. This difference is most probably due to the interaction between the polymer matrix and filler particulates. Since the segmental mobility of the chains near the filler particles is reduced, the $T_g$ of the composites increases.

Thermograms of the gypsum powder shows only one step (onset = 107.55°C) related to hydration water, and there is no interference with the other steps related to the polymer or the composite decomposition. As it was mentioned at 20 kGy the polyester–styrene resin is solidificated [Ajji, 2005]. After hardening the polyester resin, a slight change in the decomposition temperature could be observed, because the polyester-styrene/gypsum composite show a loss of 5 and 20% at 200 and 340°C, respectively, which are comparable with polyester-styrene resin (loss of 2 and 20% at 200 and 360°C, respectively).

Thermograms of the gypsum powder shows only one step (onset = 107.55°C) related to hydration water, and there is no interference with the other steps related to the polymer or the composite decomposition. As it was mentioned at 20 kGy the polyester–styrene resin is solidificated [Ajji, 2005]. After hardening the polyester resin, a slight change in the decomposition temperature could be observed, because the polyester-styrene/gypsum composite show a loss of 5 and 20% at 200 and 340°C, respectively, which are comparable with polyester-styrene resin (loss of 2 and 20% at 200 and 360°C, respectively). The decomposition temperature of the polyester-styrene/gypsum composites decrease in presence of the inorganic fillers. Furthermore, the filler seems to have influence on the mechanism of thermal degradation of the polymer. This is a generally observed behavior, that irrespective of the amount and type of filler, the inorganic particles decrease the thermal stability of the polymer composites. The main reason for inducing thermal instability is believed to be an indirect one, improved and effective heat transfer to the polymer phase through the dispersed inorganic phase.
In Poly(methyl acrylate)/phosphate composites the total polymerization conversion is achieved with a dose of 10 kGy of $^{60}\text{Co}$ gamma radiation at room temperature. The composites were prepared by converting the liquid monomer/filler systems into polymer by gamma irradiation [Ajji & Alhassanieh, 2011]. A 10 kGy dose is a little higher than the necessary dose for achieving a total polymerization conversion in order to avoid any uncertainty in the bulk of the samples.

The glass transition temperature, $T_g$ of Poly(methyl acrylate)/phosphate composite is higher than the $T_g$ of the pure poly(methyl acrylate); $13 \pm 3^\circ\text{C}$ versus $8 \pm 3^\circ\text{C}$, respectively, when both are irradiated at 15 kGy. This difference can be explained with the interaction between the polymer matrix and filler particulates (phosphate particles). Since the segmental mobility of the chains near the filler particles is reduced, and thus the $T_g$ of the composites increases. This behavior has also been observed and documented in other composite systems; the increase in the $T_g$ has been explained on the basis of reduced mobility of molecular segments in the vicinity of the filler particulates.

The presence of polymer chains surrounding phosphate particulates leads to a shielding of the phosphate particles, and consequently to a higher element ratio incorporated in the solid phase. Thus such polymer/composite systems could be considered for using as storage medium for radioactive waste of the studied radionuclides.

For non-irradiated polyester samples a 5% is loss of its initial weight at 260$^\circ\text{C}$, and for irradiated samples at 295$^\circ\text{C}$, while for the polyester-cement composite samples at 395$^\circ\text{C}$. So, the polyester-cement composite has higher thermal stability than the irradiated polyester. This is attributed to chemical reaction of the polyester and cement constituents under the effect of gamma irradiation [Ismail et al., 1998]. At higher decomposition temperatures (500$^\circ\text{C}$) there is no significant difference in thermal decomposition of non-irradiated and irradiated polyester (weight loss about 90%), while for polyester-cement composite is lower.

The break down stress of the polyester-styrene/gypsum composite is lower than the pure polyester–styrene resin when irradiating from 10 to 320 kGy. The values in both cases increase when the radiation dose augment too. The pure polyester-resin varies from 6.5 to 9.0 MPa while the polyester-styrene/gypsum composite varies from 2.0 to 3.6 MPa, it means a maximum difference of 225% [Ajji, 2005].

Such behavior is due that the gypsum (filler) has lower tensile strength than that of the polymer; and the increase of the cross-link density, which increases with increasing the irradiation dose and thus the tensile strength. This difference can be explained considering that only the polymer chains (but not the inorganic filler particles) can build cross-links between the chains.

The hardness percentage is not affected significantly by gamma irradiation; for the pure polyester-resin the percentages vary from 88 to 89.5 MPa and for polyester-styrene/gypsum composite from 91 to 92 MPa.

By solidifying concrete, water is evaporated and cavities are formed in concrete. These cavities are gas pores that cannot rise to the surface of concrete and will be caught on it. More pore formation in the concrete implies diminution on its strength. It is possible to minimize the micro pores by radiation of concrete during solidification. Because as the first micro pores have been filled by water. So, when gamma-ray interacts with water molecules,
the hydrogen moves to surface of concrete and the OH participates on Alkali-Silica Reaction (ASR) [Rezaei-Ochbelagh et al., 2010]. By this way, micro pores can be deleted. Therefore, if concrete is radiated during drying process, its strength will increase. Moreover, in the case of a concrete structure with microscopic bubbles, there is a difference in radiation intensity when the ray passes through concrete with air-filled bubbles and without that. SEM micrographs show that concretes without sand are less dense than those with sand. Moreover, the irradiated specimens are denser as compared to the non-irradiated ones.

Alkali-silica reaction in concrete is one of the slow chemical reactions. This slow reaction causes severe deterioration of concrete. Nuclear radiations make the aggregate ASR-sensitive and the deterioration of concrete can emerge long after the irradiation. It is therefore important to know the effect of nuclear radiation on the reactivity of aggregates to alkaline solution.

The compressive strength of concrete was measured against gamma radiation for two types of concretes (with and without sand). The specimens were irradiated with $^{137}\text{Cs}$ source, with a dose rate of 0.12 Gy/day. The compressive strength of irradiated concrete is more than non-irradiated concrete: 155 vs 241 kg/cm$^2$ for irradiated concrete with sand, and 145 vs 273 kg/cm$^2$ for concrete without sand [Rezaei-Ochbelagh et al., 2010].

4. Polymer concrete irradiated by gamma particles

Studies on the effects of gamma ionizing radiation on the curing process and on final properties of polymer concrete are ongoing. Developments include the effects on the mechanical properties. Our developments regarding the influence of fiber reinforcements on polymer concrete and the different behaviors based on the components (polymer resin and mineral aggregates) [Martínez-Barrera et al., 2007; Martínez-Barrera et al., 2008a; Bobadilla-Sánchez et al., 2009; Martínez-Barrera et al., 2009; Martínez-Barrera et al., 2008b; Martínez-Barrera et al., 2010].

In principle one can obtain high compressive and flexural strength, high impact and abrasion resistance, lower weight and lower costs. In general, 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$_2$).

The influence of polymeric fibers has been established. 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. 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.

The Young’s modulus $E$, can be a defining measure of whether one will obtain a ductile or more brittle concrete. Excepting only polymer concrete with marble and calcium bentonite, the values are higher than the standard value for polyester-based polymer concrete. Moreover, the improvement above that standard is notable: a) 143 % for polymer concrete with SiO$_2$, b) 141 % for polymer concrete with CaCO$_3$, and c) 120 % for polymer concrete with CaCO$_3$+SiO$_2$. Generally the higher the gamma irradiation the higher the Young’s modulus and the harder the polymer concrete becomes.
Our studies are summarized in Figures 6 to 11. In Figure 6 is shown the compressive strength of PC compounded with unsaturated polyester resin (UPR) and one or two mineral aggregates, covering gamma doses between 50 and 150 kGy; values for specimens of 100% resin are also shown.

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 when using Marble + Calcium Bentonite (M+CB) aggregates. Intermediate values are found when using Marble aggregates. The standard value of compressive strength for polyester-based PC is 70 – 80 MPa [Martínez-Barrera et al., 2008a]. Thus, considering all PCs the maximal improvement percentage on compressive strength is 68% respect to standard values. Moreover, the values for resin are comparable with those for PC with CaCO$_3$. Such resin could be used for certain applications.

![Fig. 6. Compressive strength of polymer concrete compounded with different mineral aggregates.](image)

With respect to fiber-reinforced PCs, Figure 7 shows that the compressive strength values increase when the gamma irradiation dose increases. Nevertheless, lower values are done when comparing with PCs without fibers (see Figure 6). Different types of fibers were used (N=Nylon, PP=Polypropylene, and P=Polyester) 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 observed for PC 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. In our studies the highest values have been found in formulations combining two mineral aggregates (CaCO$_3$ and SiO$_2$) and one fiber. Thus the compressive strength depends on the material type, that is to say either rigid or elastic.
Gamma Radiation as a Novel Technology for Development of New Generation Concrete

Another important mechanical feature of the PCs is related to the compressive strain at the yield point, as seen in Figure 8. The highest compressive strain values are for PC with Marble. Except PC with SiO₂ all specimens have higher values respect to the standard values reported in the literature (0.01 mm/mm) [Martínez-Barrera et al., 2009b]. On the other hand, lower values are observed for PC containing SiO₂. Different phenomena are observed, for example for certain PCs specimens the values increase up to a certain dose and afterward decrease (PC with CaCO₃, PC with M+CB 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.

Fig. 7. Compressive strength of fiber-reinforced polymer concrete compounded with different mineral aggregates.

Fig. 8. Compressive strain at yield point of polymer concrete compounded with different mineral aggregates.
In the case of fiber-reinforced PCs, the compressive strain values increase notably for specimens with two mineral aggregates rather than just one (Figure 9). Something notable is that when comparing these compressive strain values to the standard value reported in the literature for PC (0.01 mm/mm) [Martínez-Barretera et al., 2009b]: a) for PC with SiO$_2$ there is 60 % improvement; b) for PC with M+CB up to 180 %, and c) for PC with CaCO$_3$ and SiO$_2$ up to 390 %. So, it is worth point out that the combination of two minerals, one fiber, and specific gamma radiation dose allows higher values of compressive strain.

![Figure 9](https://www.intechopen.com)

Fig. 9. Compressive strain at yield point of fiber-reinforced polymer concrete compounded with different mineral aggregates.

A third mechanical feature studied was the Young’s modulus. Excepting only PC with M+CB, the values are higher than the standard value for polyester-based PCs, namely 6.7 GPa (see Figure 10) [Tavares et al., 2002]. Moreover, the improvement above that standard is notable: a) 139 % for PC with SiO$_2$, b) 122 % for PC with CaCO$_3$, and c) 108 % for PC with CaCO$_3$+SiO$_2$. Generally the higher the gamma irradiation the higher the Young’s modulus and the harder the PC becomes.

![Figure 10](https://www.intechopen.com)

Fig. 10. Young’s Modulus of polymer concrete elaborated with different mineral aggregates
In the case of fiber-reinforced PCs, the behavior of the Young’s modulus is significantly varied (Figure 11). The PC with SiO$_2$ has higher values with respect to the standard reported for polyester-based PCs (6.7 GPa) [Tavares et al., 2002]. Nevertheless, it is possible to obtain low values for PCt with CaCO$_3$+SiO$_2$, 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 PC, which may be desirable for certain applications. For the PC with combined SiO$_2$ and CaCO$_3$ the irradiation has little effect, likely due to competing interactions and effects in these materials.

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

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.

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6. References


This book brings new research insights on the properties and behavior of gamma radiation, studies from a wide range of options of gamma radiation applications in Nuclear Physics, industrial processes, Environmental Science, Radiation Biology, Radiation Chemistry, Agriculture and Forestry, sterilization, food industry, as well as the review of both advantages and problems that are present in these applications. The book is primarily intended for scientific workers who have contacts with gamma radiation, such as staff working in nuclear power plants, manufacturing industries and civil engineers, medical equipment manufacturers, oncologists, radiation therapists, dental professionals, universities and the military, as well as those who intend to enter the world of applications and problems of gamma radiation. Because of the global importance of gamma radiation, the content of this book will be interesting for the wider audience as well.

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