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Recycled cellulose from Tetra Pak packaging as reinforcement of polyester based composites

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HIGHLIGHTS

- Polymer concrete with waste cellulose from Tetra Pak packaging was elaborated.
- The effects of gamma radiation on compressive and flexural properties were studied.
- The highest mechanical performance is obtained with 2 wt% of waste cellulose from Tetra Pak.
- The lower gamma dose provides the highest compressive strength.
- Improvements on the compressive and flexural strength were obtained at irradiation dosages of 100 and 200 kGy.

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ABSTRACT

Addressing the environmental problems caused by waste generated by Tetra Pak packaging, in this work, polyester based composites with 80% of polyester resin and 20% of silica sand were elaborated; where the silica sand was partially replaced by recycled cellulose from waste Tetra Pak containers at concentrations of 1, 2, 4 and 6% by weight. Both recycled cellulose and composite specimens were subjected to ionizing radiation process by using gamma rays. The results show improvements on the mechanical properties (compressive and flexural strength as well as modulus of elasticity) of the composites when they are irradiated at 100 and 200 kGy. Such improvements can be related with the structural modifications caused by gamma irradiation on the cellulose fibers, including changes in the morphology and the crystallinity; which were analyzed through to SEM, IR and XRD techniques.

1. Introduction

Polyester based composites are the result from polymerization of the polyester resin mixed with a mineral aggregate. In this case, the polymerized monomer acts as binder for the mineral aggregates. Precast polyester composites have been used to produce a variety of products like acid tanks, manholes, drains, and highway median barriers. Special features of polyester composites can be an excellent bond agent between cement composite and steel structures, as well as repairing material. Moreover, they show fast curing, improved properties including compressive strength, specific stiffness, vibration damping, durability, as well as ability to form complex shapes, and resistance to chemicals and corrosion [1–4].

Few studies have been reported regarding the effect of fibers as reinforcement of polyester composites. Such fibers include steel, glass, carbon or polyester at different concentrations. Fiber reinforced polymers (FRP) have numerous advantages, including excellent corrosion resistance, high fatigue resistance, low thermal expansion coefficient, and to have lightweight. Moreover, they

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have high specific stiffness and an equally high specific strength in the direction of fibers alignment [5–7].

For solving high demand of construction materials, some strategies are been considered, mainly in the development of new materials based in the use of large amounts of raw, waste or recycled materials, either non-modified or structural modified. Moreover, implementation of green-laws in several countries has generated renewed research interest in eco-friendly composites materials.

Different investigations focused on the use of waste or recycled materials in composites have been developed in the last two decades. Reis [8] added recycled textile fibers to polymer composites manufactured with polymer resin and sand, for improving of their mechanical properties. Smoother failure was obtained, unlike brittleness failure for unreinforced polymer composites. Waste polyurethane formaldehyde (PUF) from packaging and recycled high density polyethylene (HDPE), as substitutes of aggregates in composites was used by Rahman et al. [9]. The results show diminution in density, porosity and water absorption when adding both waste materials. Nevertheless, such low density allows that modified composite can be used in non-load bearing structures and floating structures. Bon-Min et al. [10] added recycled PET fibers (obtained from PET packages) to composites for controlling shrinkage cracks and improving of structural ductility, under normal environmental conditions.

Cellulose is the most abundant, inexpensive and readily available carbohydrate polymer in the world; it has attracted the attention of research community all around the globe. Cellulose is traditionally extracted from plants, having normally branches with hemi-cellulose and lignin has to undergo unhealthy chemical process with harsh alkali and acid treatment. Its intrinsic properties include biodegradability, easy availability, environmental friendliness, flexibility, easy processing and impressive physical and mechanical properties.

Cellulose fibers are playing an important role in a number of applications due to their inherent eco-friendly advantages since the last few decades. They are being explored as the potential alternatives to traditional synthetic fibers for diverse applications with particular emphasis as green reinforcement. Frequently, they are used as the reinforcement component in polymers to add the specific properties in the final product. Moreover, cellulose fibers and their respective polymer composites offer a number of advantages over conventional materials such as considerable toughness, flexibility, easy processing, recyclability and eco-friendliness [11].

Increasing demand on derivatives of plant cellulose has increased wood consumption as raw material, causing deforestation and global environmental issue. Fortunately, different ways to recycle cellulose from products made with cellulose (boxes, bags, containers and office supplies, among others), are being attended [12]. Natural fibers "in natura" were also used in different quantities as polymer mortars reinforcement. Coconut, sugar cane and banana waste were added with excellent results in resistance to crack propagation [13].

Three main effects happen when a material is exposed to ionizing radiation (as gamma rays are): a) cross-linking or reticulation, b) degradation or scissioning, and c) grafting. Physical and chemical modifications on the chemical structure of each polymer depend on the amount of absorbed energy per unit mass (dosage), and the irradiation conditions (either in air or inert atmosphere). Such modifications have repercussion on their mechanical properties [14–17].

In this work recycled cellulose fibers from waste Tetra Pak packaging and gamma irradiation were used for improvement of the mechanical properties of polyester based composites. The cellulose fibers where used as a partial substitute of silica sand in the composites.

2. Experimental

2.1. Materials

Polyester composites (40 × 40 × 60 mm), were made with unsaturated polyester resin, silica sand and cellulose fibers from waste Tetra Pak beverage packaging. The resin (orthophthalic) was provided by Reichhold Company and marketed under the name Polylite 32493-00™. Silica sand (available from GOSA™) with uniform granulometry had an average diameter of 245 μm. As catalysts for curing resin, methyl ethyl ketone peroxide (MEKP) was used.

2.2. Polymer composite elaboration

Three different kinds of specimens were studied: Type I, composites without cellulose fibers (called by us as Control); Type II, composites with cellulose fibers; and Type III, composites with cellulose fibers and post-cured by gamma irradiation.

Curing of each specimen was at 20.0 ± 3.0 °C for 24 h. In the case of the specimens type III, in a first stage, they were cured by using MEKP catalyst, and after were exposed to gamma irradiation for a second cured process, which is a common technique for curing of polymers, which having advantages on the improvement of physical and chemical properties of them.

3 specimens without cellulose (Type I) were elaborated; 12 specimens corresponding to each fiber concentration (Type II), is to say, (3 units) × (4 different concentrations) = 12 specimens; and 60 specimens (Type III), corresponding to 3 units) × (4 different fiber concentrations) × (5 different dosages), i.e. 3 × 4 × 5 = 60 specimens.

The silica sand was partially replaced by recycled cellulose in concentrations of 1, 2, 4 and 6 wt%, as it is shown in the Table 1.

2.3. Gamma irradiation

Composites (shown in the Table 1), were irradiated at different dose (from 100 to 500 kGy), in air atmosphere at room temperature, by using an industrial irradiator JS-6500 which works with pencils of cobalt 60 (^{60}Co), of 5.2 years of life in average. According to literature, dosages up to 500 kGy are enough for to produce chemical modification in polymers.

The effect of cellulose fibers on the mechanical performance of polyester based composites, can be evaluated directly from results of specimens type II, but the effect of gamma irradiation on such specimens, can be related with modifications of both polyester resin and cellulose fibers. Thus, we decided study in a separated experiment, the effect of gamma irradiation on cellulose fibers through to analyzing its morphology, crystallinity and chemical structure.

2.4. Mechanical tests

After irradiating process, composites were subjected to compressive and flexural test in a Controls™ Universal Testing Machine

Table1
Polymer composite formulation.

Lot Code	Resin (%)	Sand (%)	Recycled-cellulose fibers (%)
PC	20	80	0
PC-1	20	79	1
PC-2	20	78	2
PC-4	20	76	4
PC-6	20	74	6

with a load cell of 30 tons. The compressive testing at a loading rate of 1.25 mm/min was done; and the three-point flexural testing was at a rate of 1 mm/min. Load-displacement curves and the maximum load for the collapse bending were recorded.

2.5. X-ray diffraction

X-ray diffraction patterns of the cellulose recycled fibers were collected on a BRUKER D8 ADVANCE diffractometer brand. The test conditions were: tube power 30 kV, Window 5–50°, and speed of 1°/min.

2.6. IR spectroscopy

Infrared spectra of the recycled cellulose fibers were measured in an IR spectrophotometer with ATR attachment and photoconductive detector Bruker brand, model Tensor 27, in the frequency range of 4000–500 cm^{-1}, in transmission mode.

2.7. Scanning Electron Microscopy (SEM)

Morphological and compositional analysis of the recycled cellulose fibers was carried out by using a Scanning Electron Microscopy (JEOL JSM-6510LV)

3. Results and discussion

3.1. Compressive strength

Mechanical properties of composites were studied according to the cellulose concentrations and gamma irradiation dosage.

Fig. 1 shows the compressive strength values of the composites Type I and II. The composites without cellulose (Type I) have a compressive strength of 90 MPa. Light increments for composites with 2 wt% were obtained, respect to composites without cellulose. Nevertheless, for higher concentrations the values gradually decreases, being 23% lower for composites with 6 wt% of cellulose, respect to control composite.

After irradiating, a well-established behavior is shown: the compressive strength values increase up to dosages of 200 kGy, and for higher dosages the values diminish gradually, as it is shown in Fig. 2. The highest value is found for composites with 2 wt% of cellulose fibers and irradiated at 200 kGy, which means 15% of

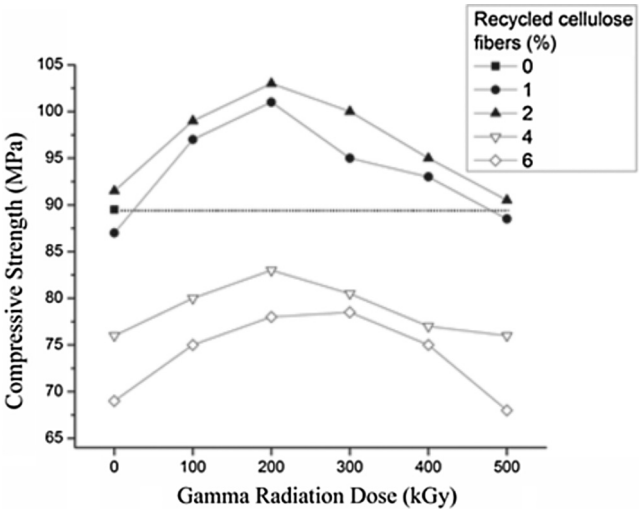

Fig. 2. Compressive strength of irradiated polyester composites.

improvement respect to non-irradiated composites. Improvements in resistance are attributed to the reticulation and cross-linking effects of gamma irradiation on the polymer matrix.

For a better understood of the behavior after irradiating, we have decided to put a straight line starting from the value for composite Type I (without fibers), for to show graphically those values above or below of the same.

According to the cellulose fiber concentrations, compressive strength values diminish when increasing the fiber concentrations. Such reduction can be attributed to the inefficient transfer of stresses between composite and recycled cellulose, which is a consequence of the poor adhesion between polymer matrix (hydrophobic) and cellulose (hydrophilic). Despite subjecting cellulose to a drying process prior to preparing composites, some moisture was remaining and acting as a release agent on the waste cellulose-resin interface, and in consequence affecting composite properties.

Compressive strength results may be related to the crystallinity of the cellulose fibers. In Fig. 3, the X-ray spectra of non-irradiated and irradiated cellulose fibers are shown (data were collected from 5 to 50° 2θ). Diffraction pattern show three mean peaks, at 2θ = 14.7°, 22.5° and 34.2°. The first one is associated with the

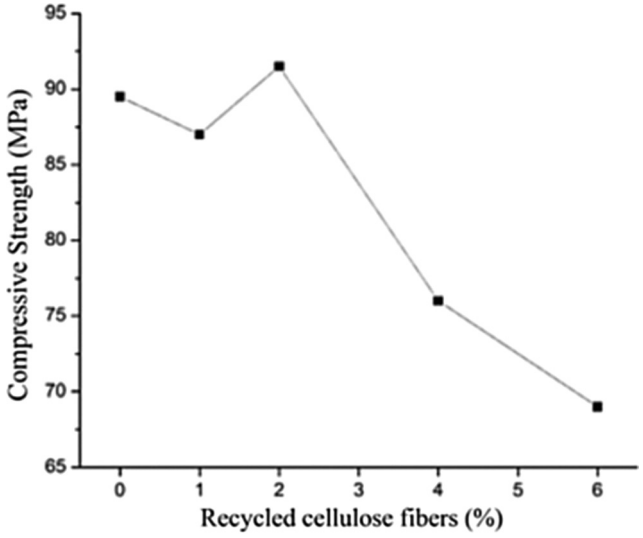

Fig. 1. Compressive strength of composites with recycled cellulose.

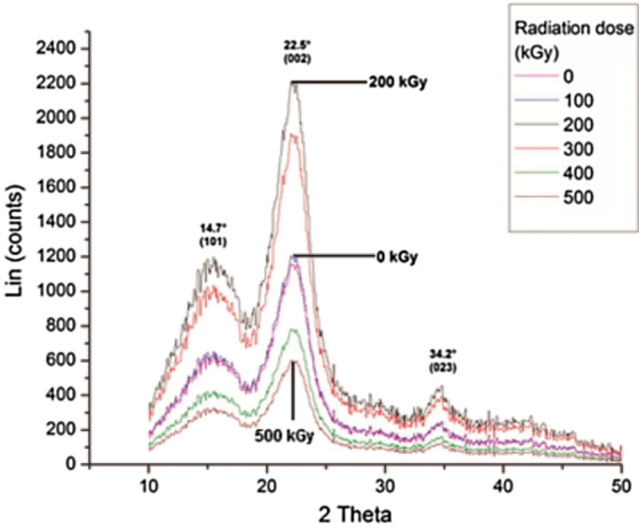

Fig. 3. X-ray diffraction pattern of cellulose.

crystallographic planes (1 0 1), while peaks at 22.5° and 34.2° (2θ), with planes (0 0 2) and (0 2 3), respectively.

The crystallinity index, Ic, was calculated by using the equation $Ic = 100 \times \frac{I_{002}-I_a}{I_{002}}$, where I_{002} is the maximum intensity of the main peak (at 22.5° 2θ) and Ia is the intensity attributed to amorphous phase (at 14.7° of 2θ). For non-irradiated cellulose, the crystallinity index was 78.3% (Fig. 4), which is lower than those for raw cellulose reported in literature (86.3%) [11].

Irradiation process produce changes in the crystallinity of the cellulose; a maximum increment is observed at 200 kGy, which is 8% higher than those for non-irradiated cellulose. Nevertheless, for higher irradiation dosages (500 kGy), the crystallinity index decreases gradually. Higher degree of crystallinity in the cellulose fibers produced at 200 kGy contribute to mechanical properties of the composite. In fact, at 200 kGy, the highest compressive strength was obtained. In general, higher crystallinity means more stiffness.

3.2. Flexural strength

Fig. 5 shows the flexural strength values of composites, which having similar behavior than those for compressive strength. Composites Type I (without fibers) have 23 MPa of flexural strength, while composites Type II (with fibers and non-irradiated), diminish their values according to fiber concentrations increase.

For irradiated composites (Type III), the flexural strength shows two-well defined behaviors. Higher values are obtained for composites with 1% or 2 wt% of cellulose fibers and irradiated at 100 kGy; while for higher concentrations (4% and 6 wt%), flexural strength decreases. It is to say, a combined process of lower irradiation energy and lower fiber concentrations allow the highest flexural values. Then, the highest value is obtained for composite with 1 wt% of cellulose and 100 kGy of irradiation dose; such value is 13% higher than those for control composite.

Diminution on the flexural strength can be attributed to the presence of some residual moisture into cellulose fibers caused at the time of mixing with the polyester resin and silica sand. Furthermore, size, shape and morphological surface of the fibers are parameters for determining mechanical properties of the composites, as it is seen in Fig. 6. For non-irradiated recycled fibers, rough surfaces with impurities (acquired during the recycling process), irregular shapes, as well as different diameter sizes are obtained.

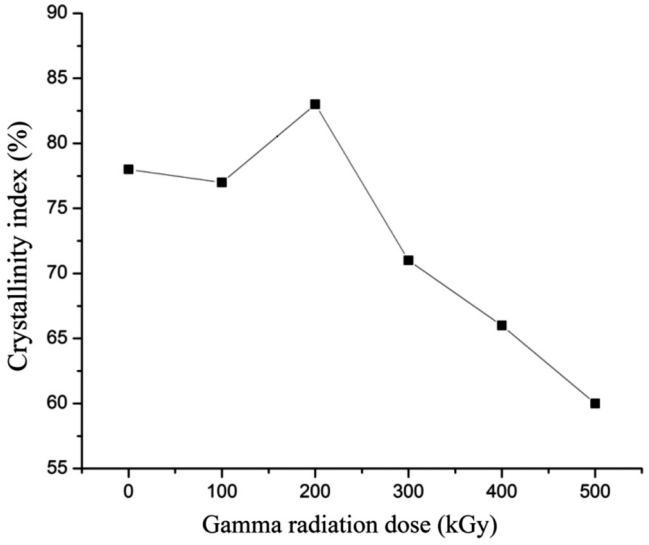

Fig. 4. Crystallinity index of recycled cellulose.

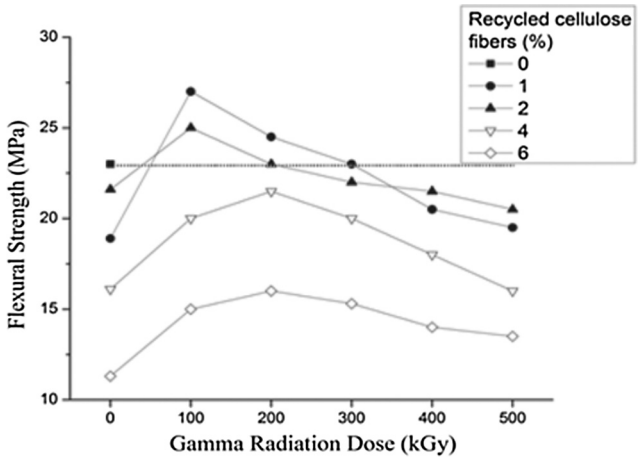

Fig. 5. Flexural strength of composites with recycled cellulose.

While for irradiated cellulose fibers dimensional and morphological changes are observed. At 100 kGy disincorporated fibers with different sizes are observed, which can be related to the highest flexural strength, is to say, more ductility of the fibers contributes to have a more ductile composite. While at 200 kGy, cellulose fibers show more soft surfaces, as consequence of the irradiation process; having the highest crystallinity degree, and thus contributes to have the highest compressive strength.

3.3. Compressive modulus of elasticity

Fig. 7 shows compressive modulus of elasticity of the composites. For composites Type I (without fibers), the value is 32 GPa. When adding cellulose fibers (composites Type II) the values increase for 1% or 2 wt%, while for higher cellulose concentrations (4% and 6 wt%), the modulus decreases considerably. Such diminution is attributed to the cellulose moisture. In fact, the absorbed water by cellulose does not provide efficient load transfer between polyester resin and the particles.

For irradiated composites, higher values are obtained at low cellulose concentration (1% or 2 wt%) and applied dose of 100 kGy. The highest value, 39 GPa, is 19% higher than value for control composite. The cross-linking effect caused by ionizing energy on the polyester resin increases the resistance and thus Young's modulus increases.

3.4. Compressive strain at yield point

Fig. 8 shows the compressive strain at yield point of the composites. In the case of composites Type I (without cellulose fibers) the value is 0.036 mm/mm. Such value increases for composites with cellulose (Type II) up to 25%; mainly for composites with 1% and 2 wt% of cellulose fibers. Such increment is due to the action of the fibers, which interrupt the crack propagation, and in consequence the deformation is greater; thus a more ductile composite is produced. Contrarily for higher concentrations of cellulose (4% and 6 wt%), deformation decreases drastically.

More significant are the results for composites with cellulose and irradiated (Type III), because the deformation increases up to 0.053 mm/mm, is to say 43% higher than those for control composites; this for irradiated composite at 400 kGy with 2 wt% of cellulose fibers. Such improvements are attributed to the effects of ionizing energy on the composites, this produces higher ductility, i.e., the composites are deformed in a sustainable way before reaching the breaking point.

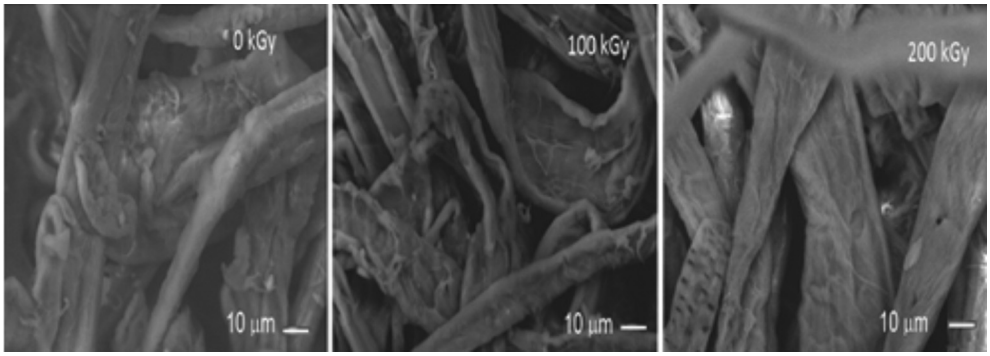

Fig. 6. SEM images of not-irradiated and irradiated cellulose fibers.

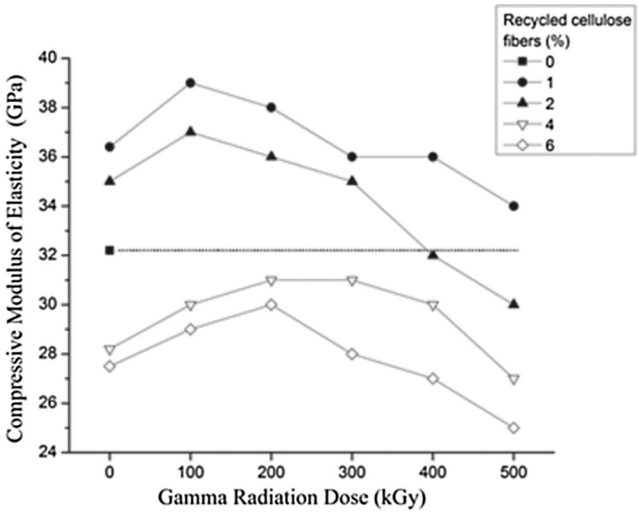

Fig. 7. Compressive modulus of elasticity of polyester based composites.

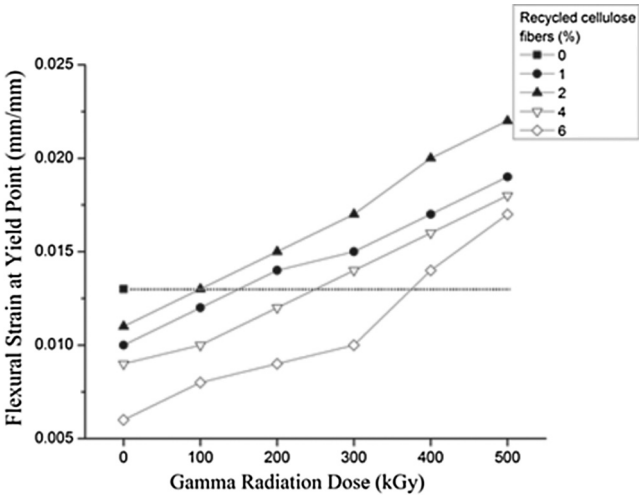

Fig. 9. Flexural strain at yield point of composites with recycled cellulose.

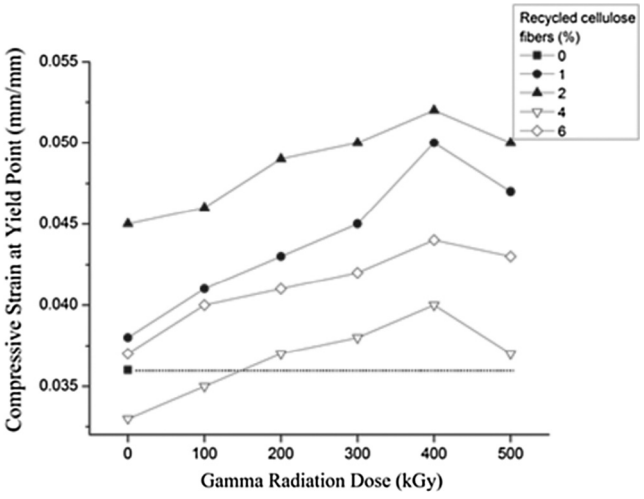

Fig. 8. Compressive strain at yield point of composite with recycled cellulose.

3.5. Flexural strain at yield point

Results of flexural tests for composites are shown in Fig. 9. Control composites (without cellulose) have a value of 0.013 mm/mm. Which decreasing when more concentration of cellulose fibers are added (Composites Type II). In the case of composites Type III, the values increase gradually according to the irradiation dose increase. The highest value is 0.022 mm/mm and it corresponds to composites with 2 wt% of cellulose and irradiated at 500 kGy. Such increment means and improvement of 69% respect to control composite. Improvements in flexural strain are attributed to the higher dose (500 kGy), which cause both scission and cross-linking effects on the polyester matrix.

Changes on the deformation of polymer composites can be related with those changes produce in the chemical structure of the cellulose fibers, which can be evaluated by using infrared spectroscopy. In Figs. 10 and 11, FT-IR spectra of non-irradiated and irradiated cellulose are shown.

The spectra ranging from 4000 to 2000 cm^{-1} is shown in Fig. 10; in this two vibrational bands are observed for non-irradiated cellulose, at 3335 cm^{-1} corresponding to O—H stretching absorption, and at 2899 cm^{-1} for C—H stretching. In the case of irradiated cellulose both peaks show higher intensity; such increment of the intensity is related to the dipole moment of the molecule, which is affected when applying gamma irradiation.

In the case of range from 2000 to 700 cm^{-1}, for non-irradiated cellulose some vibrational bands are observed at: 1030 cm^{-1}corresponding to absorption of water; 1370 cm^{-1} to OH flexural vibration; and 1640 $cm^{-1}$to C—O stretching vibration. After irradiating, the intensity of each band has lower or higher values respect to those for non-irradiating one. For dosages from 100 kGy to 400 kGy the intensity values are lower; while for irradiation dose of 500 kGy an opposite behavior is obtained with higher intensity.

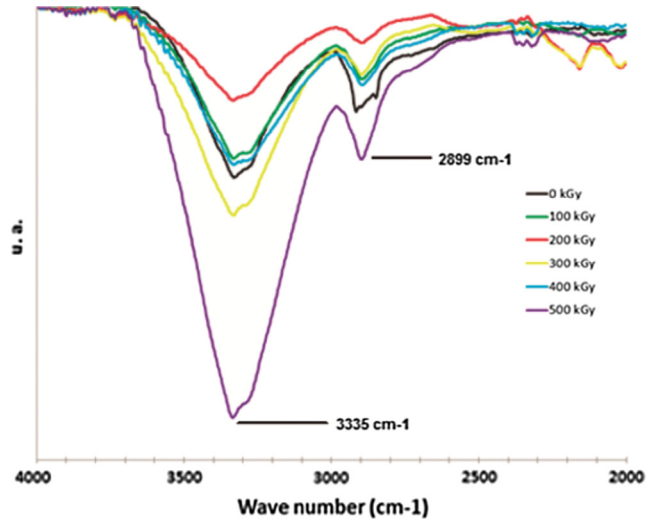

Fig. 10. FT-IR spectra of non-irradiated and irradiated cellulose (from 4000 to 2000 cm^{-1}).

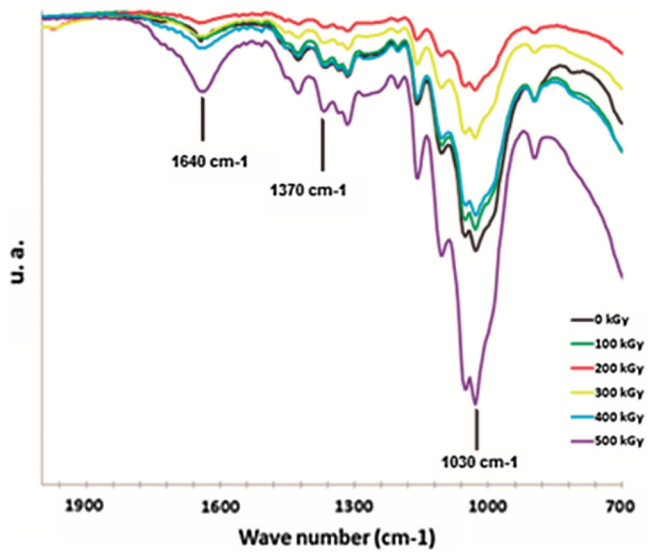

Fig. 11. FT-IR spectra of non-irradiated and irradiated cellulose (from 2000 to 700 cm^{-1}).

4. Conclusions

Recycled cellulose fibers and gamma irradiation are adequate tools for improvement of the mechanical properties of polyester based composites. In general, a combined process of lower irradiation energy, and lower fiber concentrations (2 wt%), allow highest values on the compressive strength, flexural strength, young modulus, as well as crystallinity degree in polyester composites. Such improvements are related to the morphological changes after irradiating, which include rough surfaces with impurities, irregular shapes, as well as different diameter sizes. While for higher recycled cellulose concentrations (4% and 6 wt%), mechanical properties decrease gradually. Highest values of each mechanical property depend on a specific irradiation dose, as follows: flexural strength and modulus of elasticity at 100 kGy; compressive strength at 200 kGy; compressive strain at 400 kGy, and flexural strain at 500 kGy.

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