Influence of electron beam irradiation on the mechanical properties of pbat/pla polymeric blend

Influência da irradiação por feixe de electrões nas propriedades mecânicas da mistura polimérica pbat/pla

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ABSTRACT

The aim of this research was to evaluate the changes in the mechanical properties of poly(butylene adipate co-terephthalate)/poly(lactic acid) (PBAT/PLA) polymeric blend after the radiation process at different radiation doses. The irradiation was performed in an electron beam accelerator, with 1.5 MeV of energy and 25 mA electric current. The samples were irradiated with doses of 5, 10, 15, 25, 50, 65 and 80 kGy. Both irradiated and non-irradiated samples were characterized by Izod pendulum impact resistance and tensile strength at rupture. The results showed an increase of 44% in relation to Izod impact resistance at a dose of 65 kGy. However, the module of elasticity decreased 56%

and tensile strength at rupture decreased 55% at the same radiation dose. In relation to elongation, significant alterations caused by electron beam irradiation was not observed. Therefore, it can be concluded that irradiated blends could be used to make environmentally friendly products, which could absorb impact energy.

Key-words: PBAT/PLA blend, electron beam, biodegradable polymers, irradiation.

RESUMO

O objectivo desta investigação era avaliar as alterações nas propriedades mecânicas do co-tereftalato de poli(adipato de butileno)/poli(ácido láctico) (PBAT/PLA) polimérico após o processo de radiação em diferentes doses de radiação. A irradiação foi realizada num acelerador de feixe de electrões, com 1,5 MeV de energia e 25 mA de corrente eléctrica. As amostras foram irradiadas com doses de 5, 10, 15, 25, 25, 50, 65 e 80 kGy. Tanto as amostras irradiadas como não irradiadas foram caracterizadas por resistência ao impacto do pêndulo de Izod e resistência à ruptura por tracção. Os resultados mostraram um aumento de 44% em relação à resistência ao impacto de Izod com uma dose de 65 kGy. No entanto, o módulo de elasticidade diminuiu 56% e a resistência à ruptura diminuiu 55% com a mesma dose de radiação. Em relação ao alongamento, não foram observadas alterações significativas causadas pela irradiação por feixe de electrões. Por conseguinte, pode concluir-se que as misturas irradiadas poderiam ser utilizadas para fazer produtos amigos do ambiente, os quais poderiam absorver energia de impacto.

Palavras-chave: mistura PBAT/PLA, feixe de electrões, polímeros biodegradáveis, irradiação.

1 INTRODUCTION

The polymeric bend of PBAT/PLA – poly(butylene adipate co-terephthalate)/poly(lactic acid), which is known commercially as Ecovio® [1,2], was the object of this research. This polymeric blend has been used at industrial scale and, therefore, it is an example of industrial development and environmental conservation, as it is composed of biodegradable polymers.

The aim of this research was to determine the mechanical properties of the PBAT/PLA polymeric blend irradiated with an electron beam at the dose of 5, 10, 15, 25, 50, 65 and 80 kGy.

The methodology adopted in this research was based upon a case study which used both qualitative and quantitative data. This data was obtained through mechanical tests of tensile strength, elongation, modulus of elasticity, impact and hardness.

Biodegradable polymers can be used to make products with an average life cycle (ranging from 1 to 5 years)[3]. Examples of these polymers can be seen in biodegradable packaging of products that need to be irradiated for commercialization. This requires the evaluation of changes in the mechanical properties of the PBAT/PLA polymeric blend based on the absorbed dose.

Biopolymer classification in relation to the environment can be observed in

Fig. *1*. In the horizontal axis the polymer is evaluated in relation to its biodegradability and in the vertical axis the raw materials of this polymer are evaluated based on whether they are renewably sourced.

Fig. 1. Classification of polymers based on environmental criteria [4]

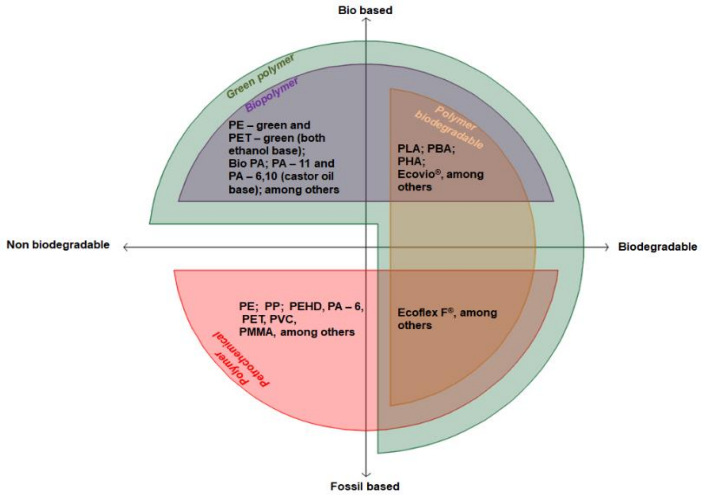
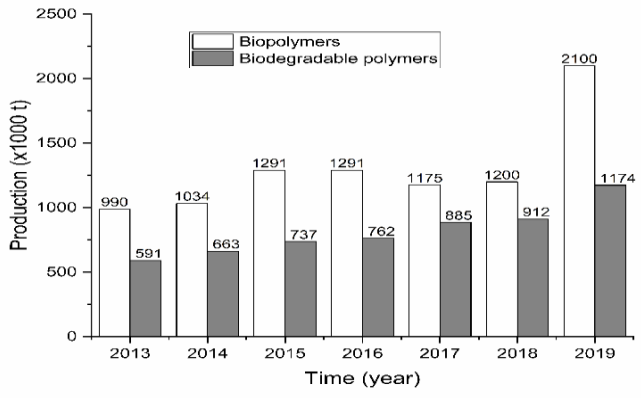


Fig. 1, the first, second and fourth quadrants represent the "green" polymers. The first and second quadrants represent the biopolymers and the biodegradable polymers are represented by the first and fourth quadrants. Finally, the third and fourth quadrants represent the petrochemical polymers. The designation as a green polymer is used to differentiate all polymers from the petrochemical polymers. When a polymer is classified as biodegradable, it should automatically be classified as a green polymer. It may also be a biopolymer if this biodegradable polymer was produced from a renewable source. Therefore, the PBAT/PLA polymeric blend polymers can be classified as both biodegradable biopolymers and green polymers. Environmental concerns may have generated a higher consumption of biodegradable polymers, and consequently an increase in the production of this type of polymer, as shown in Fig. 2, where the white bars represent the world production of biopolymers and the grey of the biodegradable polymers.

Fig. 2. World production of biopolymers and biodegradable polymers[5,6]



There has been increase of 112% in the world's production of biopolymers from 2013 to 2019. Biodegradable polymers represented 37% of the world's production of biopolymers in 2013. However, in 2019, biodegradable polymers accounted for 56% of the world's production[5].

For PBAT its world production in 2019 was 300,000 t, and for PLA was 334,000 t, which, respectively, represent approximately 25% and 28% of the world's production of the biodegradable polymers in this year. Increases in production were due the increased market competitiveness of both biodegradable polymers in relation to to other polymers[7].

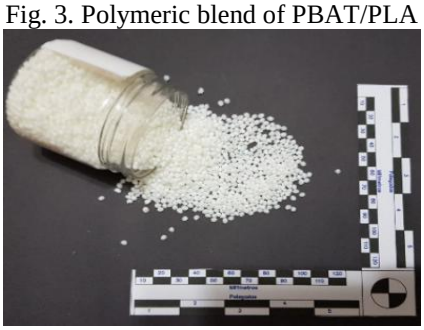
However, because prior research has indicated that irradiation may effect the mechanical properties of the polymeric blend PBAT/PLA, a systematic evaluation of these effects is warranted.

2 MATERIALS AND METHODS

2.1 MATERIALS

The polymeric blend of PBAT/PLA material analyzed in this study was composed of 55% of PBAT and 45% of PLA. It has a translucent semi-crystalline structure and good thermal stability up to 230ºC. This blend was obtained using a twin-screw extrusion[1] [2]; the polymeric blend is shown in Fig. 3.

Fig. 3. Polymeric blend of PBAT/PLA



The polymeric blend was in pellet format, as shown in Fig. 3 because of this format faculty the thermal process.[8,9]

2.2 METHODS

The materials and the parameters used in irradiation, injection and testing of PBAT/PLA are as follows:

2.2.1 Injection

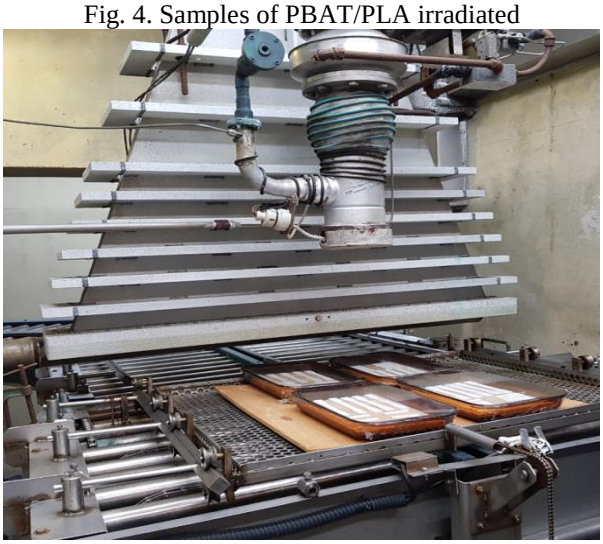
The samples were injected using the Hatian PL 1600 injection molding machine and the injection parameters were based on a mold temperature of 45ºC, cylinder temperature of 150°C, injection pressure of 40 bar, injection time of 3 s, injection flow 50 cm^3/s and a boost pressure of 20 bar. The samples for the tensile strength test were injected in accordance with the ASTM D638-14: Standard test method for tensile properties of plastics[10], and the samples for the impact test were in accordance with ASTM D256-10E1: Standard test methods for determining the Izod pendulum impact resistance of plastics[11].

2.2.2 Irradiation

The samples were irradiated with an electron beam. This process was performed using an electron accelerator model DC1500/25/4 – JOB 188, energy of 1.5 MeV, electric current of the beam of 25 mA, a scan of 1200 mm and power of 150 kW.

The samples in the electron accelerator are accommodated in trays, as shown in Fig. 4.

Fig. 4. Samples of PBAT/PLA irradiated



The irradiation parameters were energy 1.437 MeV, beam width of 1000 mm, the electric current of the beam of the 3.26 mA, the dose rate of 13.35 $kGy.s^{-1}$ and the dose per tray pass was 5 kGy. The samples were irradiated at the absorbed doses of 5, 10, 15, 25, 50, 65 and 80 kGy.

2.2.3 Mechanical tests

Tensile strength tests were performed using the mechanical universal test machine model INSTRON 5567 installed in the Radiation Technology Centre of the Nuclear and Energy Research Institute – IPEN, Sao Paulo, Brazil. The test conditions were a temperature of 20ºC, relative humidity of 70% and speed of 100 $mm.min^{-1}$.

The equipment used for the impact strength tests was a NZ Philpolymer, model XRL – 400 – Izod. The test conditions were at a temperature of 23±2ºC, relative humidity 50±10% and the pendulum of the 0,1 J.

For the hardness test, a digital durometer model Shore D – Novotest TEC-35540D was used, an instrument indicated for tests of rubber and rigid polymers, as exemplified by the polymeric blend of PBAT/PLA. This test was performed at a temperature of the 23±2ºC[12]. For all of the mechanical tests, four test bodies were used.

3 RESULTS AND DISCUSSION

The results of the tests of tensile strength, impact strength resistance and shore D hardness are presented. The error bars represent one standard deviation from the average.

3.1 TENSILE STRENGTH TESTS

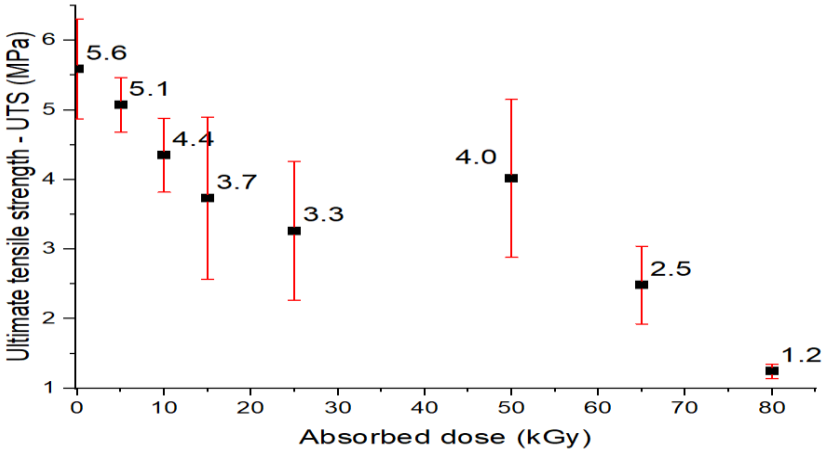
A variation of 55% was observed between the smallest elongation, which was at an absorbed dose of the 25 kGy, and the largest elongation, at a dose of 10 kGy. However, the average elongation of 2.5% was practically constant. A fragile fracture in the test bodies was observed.

For the dose of 10 kGy an elongation of 35% was observed, greater than that of the non-irradiated material, but at 25 kGy the elongation was 13% less than the non-irradiated polymeric blend of PBAT/PLA.

In relation at ultimate tensile strength, a reduction of 78.6% was observed in the polymeric blend irradiated at a dose of 80 kGy, as shown in

Fig. 5, where the horizontal axis represents the absorbed dose and the vertical shows the ultimate tensile strength.

Fig. 5. Ultimate tensile strength of PBAT/PLA polymeric blend as a function of absorbed dose

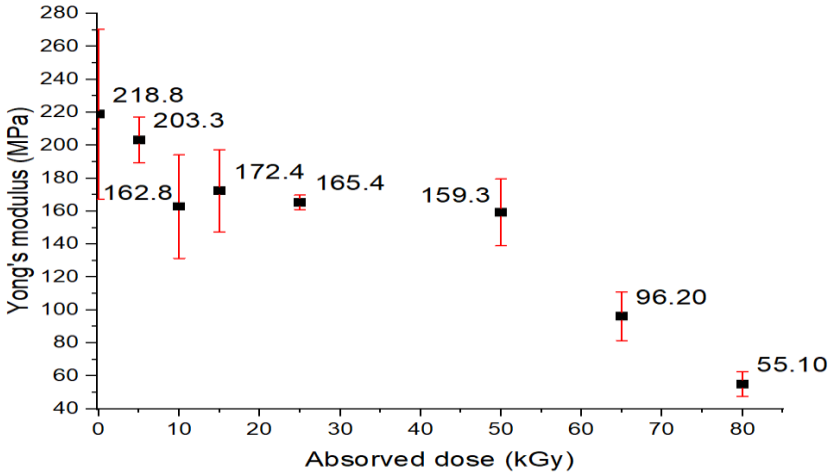


Therefore, at a dose of 80 kGy, the ultimate tensile strength reduced significantly in relation to non-irradiated material.

Yong's modulus can been used to observe a reduction of 74.8% in this propriety when the blend was irradiated at absorbed dose of 80 kGy, as show in

Fig. *6*, where the horizontal axis shows the absorbed dose and the vertical represents Yong's modulus.

Fig. 6. Yong's modulus of PBAT/PLA polymeric blend as a function of absorbed dose

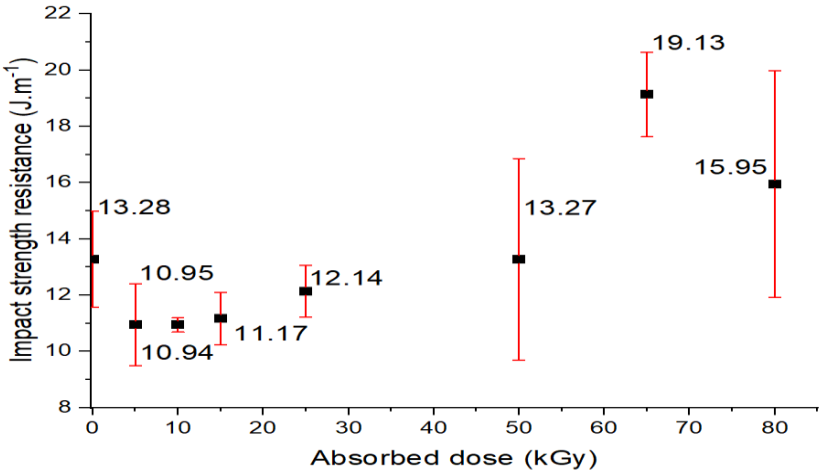


The tendency of Yong's modulus for the range of dose studied was to decrease with incremental absorbed dose.

3.2 IMPACT STRENGTH RESISTANCE TEST

An additional mechanical test was necessary for characterizationof impact strength resistance. A reduction of 21.5% was observed in an impact strength resistance tests in which the polymeric blend of PBAT/PLA was irradiated at an absorbed dose of 5 kGy. But when this material was subjected to a dose of 80 kGy, 43% increment in resistance was observed in relation to material irradiated with a dose of the 5 kGy, as shown in **Erro! Fonte de referência não encontrada.**, where the vertical axis represents the impact strength resistance and the horizontal shows the absorbed dose.

Fig. 7. Impact strength resistance of PBAT/PLA polymeric blend in function of absorbed dose



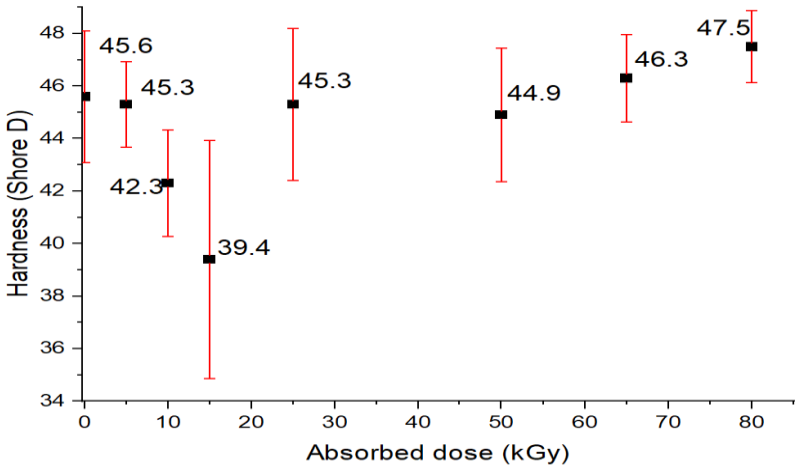
A decrease of 16.2% was observed in impact strength resistance tests in which a polymeric blend was irradiated with a dose of 80 kGy in relation to the dose of 65 kGy, possibly because the ionizing radiation could be favoring the degradation process. However, at a dose of 65 kGy an increase of the 44.1% was observed in impact strength resistance in relation to non-irradiated material. This dose may favor the cross-linking process.

3.3 SHORE D HARDNESS TEST

A variation of 20.6% was observed between the lowest hardness, which occurred at an absorbed dose of the 15 kGy, and the greatest hardness, which can be observed in the dose of the 80 kGy, as shown in

Fig. *8*, where the horizontal axis represents the absorbed dose and the vertical shows the hardness.

Fig. 8 Shore D hardness of PBAT/PLA polymeric blend in function of absorbed dose



The variation in hardness between the irradiated material and the material that absorbed a dose of ionizing radiation of 80 kGy was approximately 4.2%, that is, practically constant.

4 CONCLUSION

The mechanical properties of the polymer blend PBAT/PLA were evaluated. A reduction of 78,6% was observed in relation to tensile strength at the highest irradiated dose of 80 kGy. There was also a reduction of 80% in Yong's modulus at this dose. A significant change in hardness was not observed at a dose of 65 kGy in relation to the non-irradiated polymeric blend. The absorbed dose of the 65 kGy was noteworthy, because at this dose, there was an increase of 43% in impact strength resistance.

Products made with the biodegradable polymer blend PBAT/PLA need to be resistant to cross-sectional demands, impact, and should have an average lifespan of 1 to 5 years. For products such as injected packaging, films for the production of tubes, plastic bags, packaging for cosmetics and food packaging, among others, it is recommended to use the polymer blend of PBAT/PLA irradiated with 65 kGy.

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