Effect of Radiation-Assisted Cure on the Functional Properties of Carbon-Epoxy Composites

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Abstract

Gamma radiation has been successfully used to improve polymer's properties. In this regard, this study aims to assess if it is possible to improve carbon-epoxy composites' mechanical and thermal properties, with potential application in aeronautics, through controlled exposition to gamma radiation. In addition, make a comparative study between post-cure irradiation and radiation-assisted cure. To accomplish this, the material is subjected to gamma radiation in different stages of the resin's cure.

The laminates were fabricated with a 3K carbon mat with 160 $g.m^{-2}$ and a two-component resin SR8200 with SD7206 hardener through wet-layup. The test specimens were cut from the laminate according to ISO 527-4/2020 and ISO 14125/2011. Finally, they were irradiated according to three irradiation methodologies: post-cure irradiation, irradiation after 2 days, and after 10 days with doses from 4 to 7 kGy. These doses were selected based on a preliminary study.

The specimens were tested through tensile and flexural testing, thermogravimetry analysis and differential scanning calorimetry. The results showed that up to 6 kGy, the three irradiation methodologies improved the thermal stability and mechanical properties without affecting molecular structural integrity due to chain-scission, compared to non-irradiated specimens.

The biggest increases registered were a 32.36 % increase in Young's modulus and a 51.23 % increase in flexural modulus for irradiation after 2 days, and an increase of 5.10 % in degradation temperature and 7.44 % in glass transition temperature for the same irradiation methodology, suggesting that radiation-assisted cure is more effective at improving the material's properties compared to post-cure irradiation.

Keywords: Radiation-assisted cure, carbon-epoxy, composites, crosslinking, mechanical properties, thermal properties

1. Introduction

The advent of composite materials that combine stiff fibers, such as carbon fiber, with high-performance polymer resins has been helping to overcome major difficulties posed by the complex design of modern aircraft (Hsissou et al., 2021). As a result, fiber-reinforced polymer composite materials are becoming the primary material for aircraft construction (Mangalgiri, 1999).

The aviation industry is the most interested and constantly adapting to integrating composites to enhance performance and safety. A profitable aviation business depends on stronger lightweight materials for their aircraft without compromising safety and reliability (Yadav et al., 2021). Modern military aircraft have over 30% of their structural weight built-in advanced composites (wings, propellers, control surfaces and radome), while modern civil aircraft already have more than 50% (Alemour et al., 2019).

Composite materials are thus becoming a trend in aircraft construction, already being increasingly used in modern civil and military aircraft but also in Unmanned Aircraft Vehicles (UAVs) (Bielawski, 2017). Following this trend, Portugal keeps up with the rest of NATO's state members and has acquired UAVs for all three branches of the Portuguese Armed Forces and qualified personnel to fly them. In parallel with the operation of these commercial UAVs, the Portuguese Air Force, through the Investigation Center of the Portuguese Air Force Academy (CIAFA), has been developing research in the conception, construction and optimization of their own UAVs, with specific characteristics adapted to their missions. Although CIAFA uses carbon-fiber-reinforced composites as one of the primary materials in the fabrication of UAVs, even so it is crucial to find new ways to reduce weight and improve the strength of the components of these unmanned aircraft (Soares, 2021).

The interest in the effect of radiation on polymer materials grew rapidly with the recognition of the potential of associated techniques to improve their physical-chemical and mechanical properties and as a testing parameter for aerospatial applications. Industries like aerospace and electronics require polymers with a specific response when exposed to radiation. Radiation-induced crosslinking and highly durable materials under radiation fields are some properties these industries are looking for when designing and developing these materials for high-demanding applications (Reichmanis et al., 1993).

Fiber-reinforced composite materials are usually cured at room temperature or with heat, but the radiation-assisted cure can significantly improve strength, curing time and process cost. In addition, the radiation-assisted cure improves the composite through polymerization and crosslinking (Cleland et al., 2003).

1.1 Objectives

This study aims to assess whether it is possible to improve carbon-epoxy composites' mechanical and thermal properties, with potential application in aeronautics, through controlled exposition to gamma radiation. The main goal is to evaluate how the radiation-assisted cure influences the treated material's final properties compared to post-cure irradiation. To accomplish this, the material was subjected to gamma irradiation in different stages of the resin's cure, and the respective thermal resistance and mechanical behavior were exhaustively evaluated.

2. Literature Review

2.1 Fiber Reinforced Composites

Fiber-reinforced polymer composites consist of high strength and modulus fibers combined with a polymer-based matrix (Figure 1). Both fibers and matrix have very different physical and chemical identities. However, when combined, they attain properties that the individual components can not attain alone. In general, fibers are the principal load-carrying members and the surrounding matrix keeps them in the desired position and orientation, acting as a load transfer mechanism between them. The matrix also protects the fibers from the environment, such as elevated temperatures, humidity and aggressive agents (oxidants, fuel lubricating greases, etc.) (Mallick, 2007).

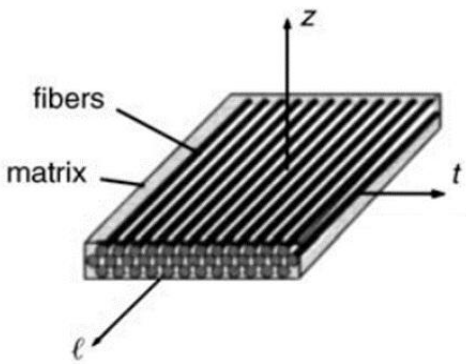

Figure 1 - Composite constitution (fibers + matrix) (Gay et al., 2002).

The most common form of fiber-reinforced composites in structural applications is called laminate. A laminate consists of series of stacked layers of fibers and matrix, consolidated in the desired thickness. Fiber orientation in each layer and the stacking sequence of different layers in

the laminate can be changed to create a range of different physical and mechanical properties (Mallick, 2007). In the case of carbon fiber, each layer or lamina has thousands of fibers along its thickness because each fiber tow comprises thousands of carbon filaments (Chung, 2010).

The number of applications for fiber-reinforced polymer composites is vast, making it difficult to quantify. For example, aircraft already have many components made of composite materials (e.g., primary structure components, control surfaces, exterior and interior components). Fiber-reinforced polymer composites are also used in other areas such as sporting goods, electronics, buildings and public works, road transports, and marine transports (Gay et al., 2003). Even though fiber-reinforced composites have countless applications, they are primarily used in aircraft and military applications for their low density to stiffness ratio and flexible design, leading to a significant weight reduction, which is critical for increasing speeds and payloads (Mallick, 2007). Carbon-fiber reinforced composites are heavily used in military aircraft, helicopters and UAVs. It is foreseen that by the end of 2025, the carbon-fiber-reinforced composites in the aerospace and defense industry will reach 1.56 billion dollars, and the UAV aircraft's value will grow exponentially until the end of that year (Yadav et al., 2021).

2.1.2 Carbon Fibers

Fibers consist of thousands of filaments with a diameter of 5 to 15 micrometers which allows them to be produced using textile machines to fabricate wovens that are then cut to fabricate composite materials. The principal fiber materials used for composite preparation are glass, aramid, carbon, boron and silicon carbide (Gay et al., 2003). These fibers are bundled together in tows which are identified according to the number of filaments they contain. Common tow ratings are 3K, 6K, 12K and 15K. The K refers to a thousand, so a 3k tow is made with 3000 filaments (Latteier, 2019).

The fibers used to fabricate laminates can be arranged in a unidirectional orientation, a bidirectional orientation or a multidirectional orientation. For unidirectional fibers, the strength and modulus reach their maximum values in the longitudinal direction of the fiber. However, these values decrease greatly in the transverse direction. Bidirectional fibers can vary their properties by using different amounts of fibers for each direction. Also, each laminate's layer may have the fibers oriented in one direction or different directions (Mallick, 2007)

Carbon fiber's advantages are their exceptionally high tensile strength to weight ratio and tensile modulus to weight ratio, low coefficient of thermal expansion, fatigue strength, and high thermal conductivity. On the other hand, their low failure strain and low impact resistance are disadvantages. In addition, high costs exclude carbon fibers from most commercial applications; they are mostly used in the aerospace industry since weight saving is more important than cost or in industries where cost is a secondary problem (Mallick, 2007)

2.1.3 Epoxy Resin Matrix

The matrix purpose in a composite material is to keep the fibers in place, transfer the stress to the fibers, provide a barrier against the environment, and protect the fibers' surface from mechanical degradation. The matrix influence on the tensile load-carrying capacity is minor on a composite, but it is important to provide lateral support to the fibers and avoid buckling under compressive loads (Mallick, 2007).

Polymer matrices can be divided into two groups, thermosetting and thermoplastic polymers. Thermoplastic polymers lose their rigidity when subjected to heat, which allows them to be reshaped under pressure, maintaining the new shape after cooling. On the other hand, thermosetting substances become permanently rigid after the molding process because they suffer permanent chemical changes that can not be reversible (Bolton & Higgins, 2014).

Epoxy is the most used polymer matrix for structural applications because of its strong adhesiveness with different fibers, excellent mechanical properties and relatively low price. Also, uncured epoxy has a relatively low molecular weight in the liquid state resulting in high molecular mobility during composite fabrication, which helps during the fabrication process since the resin can quickly spread and impregnate through the carbon fibers (Chung, 2010). Curing is initiated by adding a curing agent, and as the curing progresses, molecules start crosslinking, forming a three-dimensional structure resulting in a solid epoxy matrix. Generally, higher crosslinking improves tensile modulus, glass transition temperature, thermal stability, and a consequent decrease in elongation at break (Mallick, 2007).

2.2 Mechanical Properties

Structural applications require mechanical properties (e.g., strength and stiffness) in the material to bear the load in the structure. Therefore, mechanical performance is fundamental to the selection of structural material. Strength, modulus and ductility can be measured in tension, compression or bending. Fiber-reinforced polymers are dominant, as structural materials, due to their high strength and low density (Chung, 2010).

The carbon-fiber-reinforced composites properties, such as bending and tension are crucial when designing a structure. These properties vary depending on the used fiber and matrix (Deokar & Visal, 2019).

Strain is defined as the change in dimension per unit length. **Stress** arises when the applied force acts perpendicular to the area of interest. The strain is **elastic** when it fully recovers from applied stress, and the material subjected to the stress does not show any permanent deformation. In most materials, the elastic stress-strain relation is linear and can be expressed by Hooke's law (Wright & Askeland, 2014):

$$\frac{\sigma}{\varepsilon} = E \tag{1}$$

where σ is the stress in Pascal (Pa), ε is the strain value (m/m), and E is the Young's modulus or modulus of elasticity in Pascal.

Permanent deformation in a material is known as **plastic** strain. The material's **yield strength** is the critical stress value that initiates the plastic deformation. The **tensile strength** is the maximum stress on the stress-strain curve, also known as **ultimate tensile strength.**

In many materials, tensile tests are sometimes hard to be performed because of superficial flaws. Often, just placing the test specimen in the grips of the tensile machine can cause cracking. An alternative to tensile testing is the bending test. The load is applied at three points, causing bending, and a tensile force acts on the test specimen opposite the midpoint causing a fracture. The bending test results are similar to the stress-strain curve, but the stress is plotted with deflection instead of strain (Wright & Askeland, 2014).

2.3 Thermal Properties

Glass transition temperature (T_g) and degradation temperature (T_{deg}) are two properties that define the thermal stability of the material's structure. Therefore, improving these properties is the key to improving the structural stability of a composite's matrix regarding its thermal behavior (Rami et al., 2010).

Thermal degradation behavior is a very important property of polymeric materials. It corresponds to a type of polymer degradation where adverse chemical changes (e.g., scission of molecular chains) occur with increasing temperature, without the simultaneous involvement of other compounds such as oxygen. Consequently, polymers may undergo chemical reactions, and

small molecular fragments can evolve in gaseous form. Consequently, there is a reduction in the mass of the material and its structural cohesion, negatively impacting the material's structural integrity and robustness (Callister & Rethwisch, 2017). Normally Thermogravimetric Analysis (TGA) monitors the weight change of a sample inside a furnace, in a controlled atmosphere, with increasing temperature. This technique gives information about the material's thermal stability (Seifi et al., 2020).

One of the most important properties of polymers is T_g. It describes the temperature region where the mechanical properties of the polymeric material change from hard and brittle to soft and rubber-like. Normally its investigated through Differential Scanning Calorimetry (DSC) analysis (Seifi et al., 2020). The softening at T_g is due to the movement of the constituent molecules, ions or atoms above T_g. Below T_g, there is insufficient thermal energy for such movements to occur. T_g is below the melting temperature (Chung, 2010).

2.4 Effects of Gamma Radiation on Polymer-based Materials

It is possible to modify material's physical, chemical and biological properties by exposing them to ionizing radiation. This process is defined as the radiation processing of materials, which can be controlled and used to develop or alter specific properties of a material. To understand the irradiation processing of materials, there is the need first to understand basic radiation physics, radiation sources and the interaction between radiation and matter (Sun & Chmielewski, 2017).

2.4.1 Ionizing Radiation

Ionizing radiation designates electromagnetic radiation or accelerated particle beams with enough energy to ionize atoms and molecules and includes α and β particles, electron beams, X-rays and gamma radiation (Ferreira, 2008). Ionizing radiation can modify the physical and chemical properties of the irradiated material. One of the main industrial applications for radiation is materials modification (polymer crosslinking) (Drobny, 2012).

2.4.2 Radiation Sources

Radiation can be defined as the emission or transmission of energy in the form of particles or electromagnetic waves through space or through a material medium. The first one includes electrons, positrons, protons, neutrons and ions; the second covers a wide wavelength range, including infrared, visible, ultraviolet radiation, X-rays, and gamma radiation, as shown in Figure 17 (Sun & Chmielewski, 2017).

The primary radiating sources for radiation modification of polymer properties include gamma-radiation from radioactive isotopes such as Cobalt-60, electron beams (E-Beam) from electron accelerators, and X-rays converted from electron beams (Makuuchi & Cheng, 2011).

Gamma-radiation produced by radioactive decay interacts with matter molecules through secondary electrons as high-energy electromagnetic radiation. The typical energy of gamma-radiation is a few hundred electron volts (eV), higher than the energy of ultraviolet (UV) light and slightly higher than X-rays. Cobalt-60 is the most commonly used radiation source for industrial applications (Makuuchi & Cheng, 2011).

2.4.3 Units and Dosimetry

In radiation processing, dosimetry measures the energy deposited in the irradiated material. There are different dosimeters for each application, which have different requirements for dose determination (Sun & Chmielewski, 2017). Polymethyl methacrylate (PPMA) dosimeters are among the most used routine dosimeters in gamma radiation processing units (Ferreira, 2008). PPMA dosimeters (Figure 2) were used in this study to measure the absorbed dose of each test specimen.

Figure 2 - PPMA routine dosimeter (Harwell Amber Perspex Dosimeter) (Soares, 2021).

Absorbed dose and the distribution of dose across the material are essential parameters for quality control of the radiation processing of materials. Absorbed dose (D) is the energy absorbed by a substance per unit mass. The SI unit for absorbed dose is Gray (Gy), which equals 1 J/kg. Dosimeters measure the absorbed dose during radiation processing (Makuuchi & Cheng, 2011).

Dose uniformity (U or DU) is another parameter to consider during radiation processing. Dose uniformity is a ratio between the maximum and minimum values of the absorbed dose (D_{max}, D_{min}). The absorbed dose per unit of time is commonly expressed as dose rate, and its unit is kGy.s^{-1} (Ferreira, 2008).

2.4.4 Interaction of Ionizing Radiation with Polymers

When gamma-radiation interacts with a polymer, its energy is absorbed, and radicals are produced, initiating various chemical reactions, such as:

- Crosslinking, where polymer chains are connected, formatting a network;
- Chain scission, where the molecular weight of the polymer is reduced.

Crosslinking and chain scission always coexist under radiation, one predominant over the other, depending on the type of polymer (degradative or crosslinking type). However, the overall effect depends on which of the two is predominant at a specific time. Typically, crosslinking improves the mechanical and thermal properties of the polymer and increases the viscosity of the polymer solution. In contrast, chain scission deteriorates the mechanical and thermal properties of the polymer (Makuuchi & Cheng, 2011). Crosslinking is the most important effect on radiation-assisted cure processes, improving the mechanical and thermal properties and the material's chemical, environmental, and radiation stabilities (Cleland et al., 2003). The crystallinity and molecular weight increase due to crosslinking causes an increase in the failure load and Young's modulus but a decrease in elongation at break because the material becomes stiffer. Since glass transition temperature is related to the free movement of the polymer's main chains, crosslinking will increase the glass transition temperature due to the high number of covalent chemical bonds formed, which results in a material with less molecular mobility (Sun & Chmielewski, 2017).

3. Experimental Methodology

3.1 Materials and Fabrication Process

The carbon-fiber/epoxy laminates used for the tensile and flexural test specimens were fabricated according to ISO 527-4/2020 and ISO 14125/2011, respectively. The laminates were fabricated with a 3K carbon mat with 160 $g.m^{-2}$ and a two-component epoxy resin SR8200 with an SD7206 hardener from Sicomin©. These materials are the ones available and most used at the Investigation Center of the Portuguese Air Force Academy and, for that reason, were the ones used for this thesis.

The fabrication process chosen was wet-layup. The first carbon layer is placed over the mold and impregnated with epoxy resin. Subsequently, new layers are then applied and impregnated over each other using a paint roller. On top of the laminates, a perforated released film is applied as well as a breather cloth allowing air circulation and absorbing excess resin. Finally, the vacuum bag is secured around the laminate with sealing tape. The laminate stayed in the vacuum bag for 24 hours under negative 50000 Pascal at an average temperature of 21ºC and 40 % of relative humidity before being unmolded.

The test specimens were cut using a Computer Numerical Control (CNC) machine. An end-mill of 3,5 mm was installed in the CNC machine and programmed to spin at 2000 RPM with a cut depth of 1 mm per passage. Following the cut, all test specimens were sanded with fine-grit (400 $grains.cm^{-2}$) sandpaper to wipe inconsistencies and give a proper finishing touch to the specimens. Finally, they were cleaned with isopropyl alcohol.

3.2 Irradiation Process

Irradiations were done in an experimental cobalt-60 gamma irradiator (PRECISA 22 at C^2TN/IST), under an inert atmosphere, at an average dose rate of 0,4 $kGy.h^{-1}$. The preliminary study regarding dose distribution done by (Soares, 2021) was used as a reference for the work developed in this thesis since the radiation geometry was identical and the dose uniformity (U) results obtained were close to 1. Equation 2 shows how the dose uniformity is calculated:

$$U = \frac{D_{max}}{D_{min}} \quad (2)$$

Dmax is the maximum dose registered, and Dmin is the minimum dose registered in the irradiated total volume.

Before irradiation, the specimens were put in a sealable plastic bag. Firstly the bags were previously deaerated with nitrogen and then evacuated with the aid of a vacuum pump and heat-sealed to guarantee the irradiation happened without oxygen present to avoid materials oxidation. Then the bags were sent for irradiation.

3.2.1 Irradiation Methodologies

A preliminary study was conducted to assess the optimal doses of gamma radiation. The dose range at which a significant improvement in composite degradation temperature was observed was selected to test the composite specimens under 3 irradiation methodologies: i) Post-cure irradiation, where the specimens were irradiated after the resin was fully cured (≥ 25 days); ii) Irradiation after 2 days of curing; iii) Irradiation after 10 days of curing.

On the one hand, exposing the material to radiation at the beginning of the curing process might improve crosslinking since the curing reaction is fed with additional energy. However, on the other hand, the polymeric chains just started forming and do not provide higher robustness to the polymeric matrix of the composite. Therefore, the radiation might compete with the hardener,

increasing the scission effect of the new crosslinked chains instead. Another point of view is that irradiating a fully cured composite might not be as efficient since the matrix is solidified and has lost molecular mobility, making the creation of new crosslinks more difficult.

3.3 Mechanical Properties

Testing the materials' properties under different loads allows the observation of their mechanical behavior, specifically, the relation between the applied force and the resulting deformation and the maximum stress which causes the material to fail. A precise characterization of the mechanical properties of materials can be made through a range of standardized testing methods, such as tensile and bending testing. The values obtained from these testing methods are used for materials development, component design, and quality assurance (Groeneveld & Elsea, 2009).

The tensile test is the most important destructive testing method in materials testing (Groeneveld & Elsea, 2009). Testing the tensile properties of materials involves gripping the test specimens with a known cross-section area in the jaws of a testing machine and putting it through a constant tensile force; the amount by which the test section length increases is measured for each force increment. This process will continue until the test specimen fails (Bolton & Higgins, 2014).

The most frequently studied bending load in materials is the three-point bending test. In this method, a test specimen supported as a beam is deflected at a constant rate until it fractures, demonstrating the relationship between a load and its elastic deformation (Groeneveld & Elsea, 2009).

3.3.1 Tensile Testing

Tensile testing was performed on an Instron model 3369, a universal testing machine with all the requirements of ISO 527-4/2020. The machine was located at *Laboratório de Mecânica Experimental* (LME) from the *Departmento de Engenharia Mecânica* of the *Instituto Superior Técnico*. It had a load cell of 50 kN installed, and the tests were performed at room temperature (15 to 20 °C) and 40 % relative humidity. The test speed was set to 2 $mm.min^{-1}$ according to ISO 527-4/2020, and data was collected at a frequency of 20Hz.

The testing machine recorded the load and displacement values for each test specimen. With these values, stress, nominal strain and Young's modulus were calculated according to ISO 527-1/2020. Equation 3 was used to calculate stress:

$$\sigma = \frac{F}{A} \tag{3}$$

where σ is the value of stress expressed in megapascal (MPa), F is the measured force in Newton (N), and A is the initial cross-sectional area of the test specimen expressed in square millimeters (mm^2).

Nominal strain is calculated when no extensometer is used, and it was calculated according to Equation 4:

$$\varepsilon = \frac{L_t}{L} \tag{4}$$

where ε is the nominal strain expressed as a dimensionless ratio or percentage; L_t is the gripping distance (gauge length) in millimeters (mm), and L is the increase of the gripping distance (displacement) in millimeters.

ISO 527-1/2020 states that the strain values used to calculate Young's modulus (E_t) must be ε_1 = 0,0005 and ε_2 = 0,0025, but in our case, these values did not allow a correct calculation of E_t since the machine was still in an adjusting process at those values. Instead, Young's modulus was calculated using Equation 5:

$$E_t = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} \tag{5}$$

where E_t is Young's modulus expressed in megapascal; σ_1 is the stress expressed in megapascal, measured at the strain value ε_1 = 0,015; σ_2 is the stress expressed in megapascal, measured at the strain value ε_2 = 0,020.

3.3.2 Flexural Testing

Tensile testing was performed on an Instron model 5566, a universal testing machine. It had a load cell of 500N installed, and the tests were performed at room temperature and 40 % relative humidity. The test speed was set to 2 mm.min^{-1} according to ISO 14125/2011 specifications, and data was collected at a frequency of 50Hz. The span (L) between the two supports is 80 mm, and their radius respects the values stated in the norm.

The testing machine recorded the load and displacement values for each test specimen. With these values, flexural stress, nominal strain and flexural modulus were calculated according to ISO 14125/2011. Equation 6 was used to calculate flexural stress:

$$\sigma_f = \frac{3FL}{2bh^2} \tag{6}$$

where σ_f is the flexural stress in megapascal; F is the load in Newton; L is the span in millimeters; h is the thickness of the specimen in millimeters, and b is the width of the specimen in millimeters.

The strain in the outer surface of the specimen was calculated according to Equation 7:

$$\varepsilon = \frac{6sh}{L^2} \tag{7}$$

where ε is the strain expressed as a dimensionless ratio or percentage; s is the displacement in millimeters; h is the thickness of the specimen in millimeters, and L is the span in millimeters.

For the flexural modulus, the deflections s' and s" must be calculated according to Equation 8:

$$s' = \frac{\varepsilon_f{}' L^2}{6h} \; and \; s'' = \frac{\varepsilon_f{}'' L^2}{6h} \tag{8}$$

where s' and s" are the beam mid-point deflections in millimeters; $\varepsilon_f{}'$ and $\varepsilon_f{}''$ are the flexural strains where $\varepsilon_f{}'$= 0,005 and $\varepsilon_f{}''$=0,0025.

The flexural modulus is then calculated according to Equation 9:

$$E_f = \frac{L^3}{4bh^3}\left(\frac{\Delta F}{\Delta s}\right) \tag{9}$$

where E_f is the flexural modulus expressed in megapascal; Δs is the difference in deflection between s'' and s', and ΔF is the difference in load F'' and the load F' at s'' and s', respectively.

3.4 Thermal Analysis

Thermal analysis (TA) is a branch of materials science that studies how materials' properties vary as temperature changes. The objective is to establish a connection between temperature and the materials' physical properties. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) are two of the most popular TA techniques. TA measures the materials' physical properties as a function of temperature and understands their mechanical and thermal histories necessary for materials development, components design, and quality control. Polymers represent one of the main areas where TA is used. (Menczel, Prime, et al., 2009).

3.4.1 Thermogravimetric Analysis

TGA is a technique in which the mass of a material sample is monitored as a function of time or temperature, in a controlled atmosphere, according to a defined heating program in a controlled atmosphere. The mass loss of a polymer-based characterized by TGA helps understand the material's composition, the extent of cure, thermal stability and its degradation kinetic (Menczel & Bruce Prime, 2008).

Testing was conducted on a TA Instruments model TGA 951 with a nitrogen (N_2) flow of 60 $ml.min^{-1}$. The samples necessary for each TGA run were collected from at least 5 different test specimens (used for mechanical tests). Part of the sample (between 7 and 15 mg) was placed on the platinum plate, and the weight, temperature and relative humidity were registered. All thermal runs departed from room temperature (approx. 21 ºC). The heating program used was:

1. Equilibrate at 30ºC
2. Ramp 10 $ºC.min^{-1}$ to 800ºC

3.4.2 Differential Scanning Calorimetry

DSC implies that comparative calorimetric information can be obtained on the sample during a linear temperature ramp. One of the major applications of the DSC technique is in the polymer field because of the easy and fast determination of the glass transition temperature, melting and crystallization temperatures, melting enthalpy, heat capacity and thermal history (Menczel, Judovits, et al., 2009).

In this work, tests were conducted on a TA instruments model DSC Q2000 with a nitrogen (N_2) flow of 60 $ml.min^{-1}$. Analysis was performed on *Tzero* hermetic type pan. The samples were weighed directly in the pans and then sealed with a lid cover in the *Tzero* press.

The thermal program used was:

1. Equilibrate at 30 ºC
2. Ramp 10 $ºC.min^{-1}$, to 150 ºC
3. Isothermal for 5 min
4. Ramp 10 $ºC.min^{-1}$, to -30 ºC
5. Ramp 10 $ºC.min^{-1}$, to 150 ºC

The first ramp at 10 $ºC.min^{-1}$, reference heating rate, to 150 ºC helps the polymer's structure reorganize, eliminating its thermal history and allowing easier identification of the respective T_g. On the second ramp to 150 ºC, the T_g value is then registered. Thermal history is common in polymers like epoxy resin which have an exothermic polymerization and reach high temperatures.

4. Results and Discussion

4.1 Preliminary study

A preliminary study was conducted to assess the optimal doses of gamma radiation, both in the radiation-assisted cure and post-cure, to be used later in radiation after 2 and 10 days and for post-cure irradiation. This study was performed through thermogravimetric analysis of

composite samples fully cured and still curing, irradiated with different doses of gamma radiation (1.5 kGy to 10 kGy). TGA curves showed that the effect of gamma irradiation on the increment of the degradation temperature of the composite, for both situations, is more pronounced in the range between 4 and 7 kGy, with its maximum effect at 6 -7 kGy. So, this dose range was selected to test the composite specimens under the 3 irradiation methodologies already stated.

4.2 Mechanical Properties

Figure 3 represents the evolution of Young's modulus and flexural modulus:

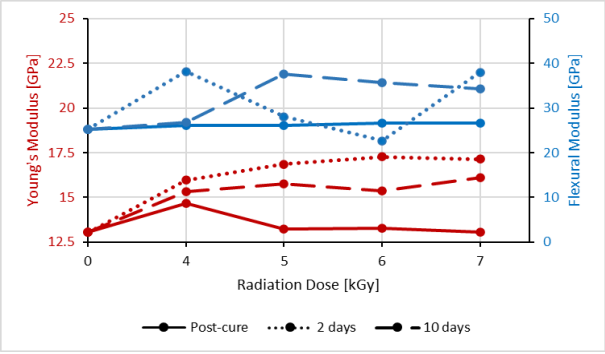

Figure 3 - Evolution of the flexural and Young's moduli at different doses through 3 irradiation methodologies.

An increase in Young's modulus was observed for all doses and methodologies compared to non-irradiated specimens. The maximum improvement registered was 32.36 % for irradiation after 2 days at 6 kGy.

The flexural modulus has a similar improvement at all doses but 5 and 6 kGy when irradiated after 2 days. The maximum improvement registered was 51.23 % for irradiation after 2 days at 4kGy. The average standard deviation (STD) for irradiation after 2 days was 6.74 %, evidencing a lack of homogeneity in these test specimens. This might explain why the irradiation after 2 days decreases between 4 and 6 kGy and then goes up again at 7 kGy.

Figures 4 and 5 represent the tensile failure load and the flexural failure load for each dose of radiation for the three irradiation processes to which the test specimens were subjected, respectively:

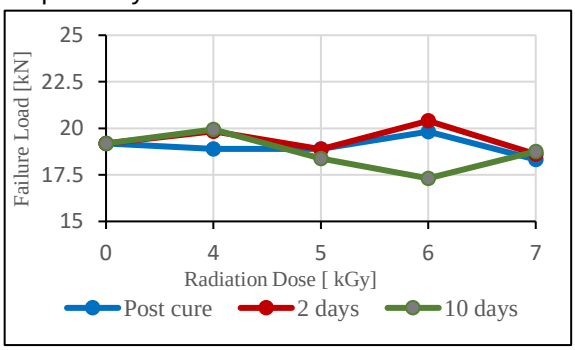

Figure 4 - Tensile failure load of the non-irradiated specimens and the specimens irradiated under three radiation methodologies at 4,5,6 and 7 kGy.

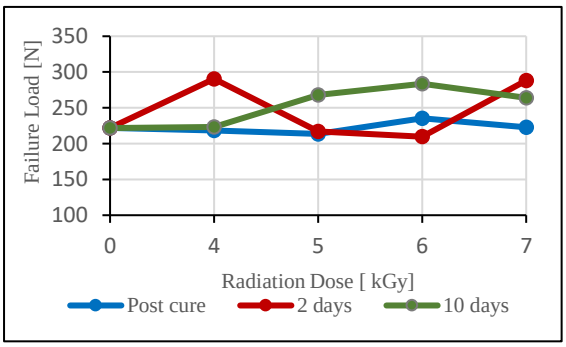

Figure 5 - Flexural failure load of the non-irradiated specimens and the specimens irradiated under three radiation methodologies at 4,5,6 and 7 kGy.

An increase in the tensile failure load was observed until 6 kGy for radiation after 2 days and post-cure irradiation. Irradiation after 10 days only improves at 4kGy. The minimum load registered was 17.3 kN at 6 kGy after 10 days; the maximum load registered was 20.4 kN at 6 kGy after 2 days. These values correspond to a decrease of 9.74 % and an increase of 6.34 %, respectively, compared to the non-irradiated test specimens. The irradiation after 10 days has the worst overall uniformity between all doses of radiation (average 6.81 % STD), evidencing a lack of homogeneity in some test specimens. The lack of homogeneity might explain why the irradiation after 10 days decreases between 5 and 6 kGy and then goes up again at 7 kGy. The same happens at 5 kGy after 2 days.

An increase in the flexural failure load was observed until 6 kGy for radiation after 10 days and post-cure irradiation. Irradiation after 2 days only improves at 4 and 7 kGy. The minimum load of 209.69 N at 6 kGy after 2 days; the maximum load of 290.47 N at 4 kGy after 2 days. These values correspond to a decrease of 3.7 % and an increase of 30.98 %, respectively, compared to the non-irradiated test specimens. Irradiation after 2 days has an average STD of 6.17 %, which evidences a lack of homogeneity in some test specimens. This might explain why the irradiation after 2 days decreases between 4 and 6 kGy and then goes up again at 7 kGy since the overall uniformity is low.

4.3 Thermal Properties

Figure 6 represents the evolution of the glass transition and degradation temperatures:

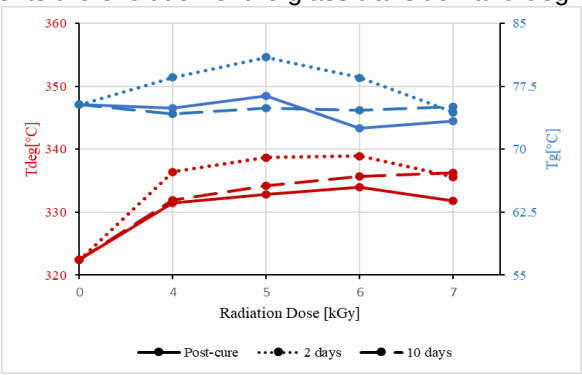

Figure 6 - Evolution of the glass transition and degradation temperatures at different doses through 3 irradiation methodologies.

The maximum degradation temperature registered was 338.9 °C at 6 kGy with irradiation after 2 days. This value translates as an increase of 16.5 °C (5.10 %). It can also be verified that for the same doses of radiation, irradiation after 2 days samples has higher values of $T_{deg,}$ followed by irradiation after 10 days and lastly by post-cure irradiation.

The maximum registered glass transition temperature was 80.94 °C at 5 kGy with irradiation after 2 days. This value translates as an increase of 5.61 °C (7.44 %). It can also be verified that for the same doses of radiation, irradiation after 2 days has higher values of T_g.

5. Conclusions

5.1 Conclusions

The mechanical and thermal tests show improvements in the carbon-epoxy composite properties that were irradiated through controlled exposition to gamma radiation compared to the non-irradiated composites. There are also improvements between the three irradiation methodologies.

The tensile testing values suggest that irradiation after 2 days provides higher values of failure load and Young's modulus compared to irradiation after 10 days and post-cure irradiation.

There is no evidence of the optimal radiation dose concerning flexural testing since it is different for each irradiation methodology. However, the dose that registered better values was 4 kGy with irradiation after 2 days. Therefore, this is the most beneficial irradiation methodology similar to tensile testing, followed by irradiation after 10 days and lastly, post-cure irradiation.

According to the TGA results, the irradiation after 2 days provides higher values of T_{deg} for most radiation doses, followed by irradiation after 10 days and post-cure, respectively.

DSC technique shows that the irradiation after 2 days provides higher values of T_g for most radiation doses. However, post-cure irradiation and irradiation after 10 days do not show significant increases in the T_g.

Comparing the mechanical and thermal analysis, it is clear that radiation-assisted cure is more effective at providing better properties to the treated material than post-cure irradiation. Particularly, irradiation after 2 days provided better properties among the three methodologies tested. Also, 5 and 6 kGy were the radiation doses that provided the higher properties values among the three methodologies tested.

The lack of structural homogeneity in the tested specimens seemed to be one of the limitations of this study. Bad dispersion of resin in the composite and some superficial flaws were clear to the naked eye. This might be related to a not efficient adhesion between the resin and the carbon fiber. In addition, the SR8200 resin and SD7206 hardener are new at CIAFA since the normally used resin was discontinued. Therefore, the fact that this resin is new was also a limitation of this study. Furthermore, this resin did not show compatibility with carbon as good as the previously used resin.

5.2 Future work

Radiation-assisted cure provided better results than post-cure irradiation, which until now was the only study made by the Portuguese Air Force related to the improvement of carbon-epoxy composites using gamma radiation. Radiation-assisted cure should be studied in depth to extend the work developed in this dissertation. This study analyzed radiation-assisted cure in the initial phase of curing and on the last day of curing (according to the cure schedule provided by the manufacturer). Analyzing this methodology in an intermediate phase might be more efficient.

The laminate fabrication process should be revised to produce a more homogenous material with fewer superficial flaws. Adding the reinforcement tabs posterior to the initial 24 hours cure might help maintain the vacuum pressure equal along the laminate, improving the overall homogeneity.

This study also showed that the adhesion between this resin and carbon fiber is not as good as the previously used resin at CIAFA. Adding an interface between the fiber and resin, such as graphene, might improve their adhesion. In addition, the influence of radiation-assisted cure in the resin, with the addition of an interface, should be tested to assess any possible improvements.

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