

DEVELOPMENT OF SEALED RADIOACTIVE SOURCES IMMOBILIZED IN EPOXY RESIN FOR VERIFICATION OF DETECTORS USED IN NUCLEAR MEDICINE

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ABSTRACT

The radioactive sealed sources are used in verification ionization chamber detectors, which measure the activity of radioisotopes used in several areas, such as in nuclear medicine. The measurement of the activity of radioisotopes must be made with accuracy, because it is administered to a patient. To ensure the proper functioning of the ionization chamber detectors, standardized tests are set by the International Atomic Energy Agency (IAEA) and the National Nuclear Energy Commission using sealed radioactive sources of Barium-133, Cesium-137 and Cobalt-57. The tests assess the accuracy, precision, reproducibility and linearity of response of the equipment. The focus of this work was the study and the development of these radioactive sources with standard Barium-133, Cesium-137 and Cobalt-57, using a polymer, in case commercial epoxy resin of diglycidyl ether of bisphenol A (DGEBA) and a curing agent based on modified polyamine diethylenetriamine (DETA), to immobilize the radioactive material. The polymeric matrix has the main function of fix and immobilize the radioactive contents not allowing them to leak within the technical limits required by the standards of radiological protection in the category of characteristics of a sealed source and additionally have the ability to retain the emanation of any gases that may be formed during the manufacture process and the useful life of this artifact. The manufacturing process of a sealed source standard consists of the potting, into bottle standardized geometry, in fixed volume of a quantity of a polymeric matrix within which is added and dispersed homogeneously to need and exact amount in activity of the radioactive materials standards. Accordingly, a study was conducted for the choice of epoxy resin, analyzing its characteristics and properties. Studies and tests were performed, examining the maximum solubility of the resin in water (acidic solution, simulating the conditions of radioactive solution), loss of mechanical and thermal properties, as well as the radioactive dose control for complete curing (cobalt irradiators). For this work was produced a source of barium-133, tests were conducted to determine the degree of homogeneity in the dispersion of the radioactive material in the matrix and immersion tests of sealed source produced to verify the leakage (ISO 9978) of the developed system, occurring obtaining a satisfactory result.

1. INTRODUCTION

The ionization chamber detectors, shown in Fig. 1, are devices widely used by nuclear medicine services, to assess the activity of the radioisotopes used in diagnostic and therapeutic purposes. The measurement of the activity of these radioisotopes must be done with accuracy because it will be injected in a patient. [1]

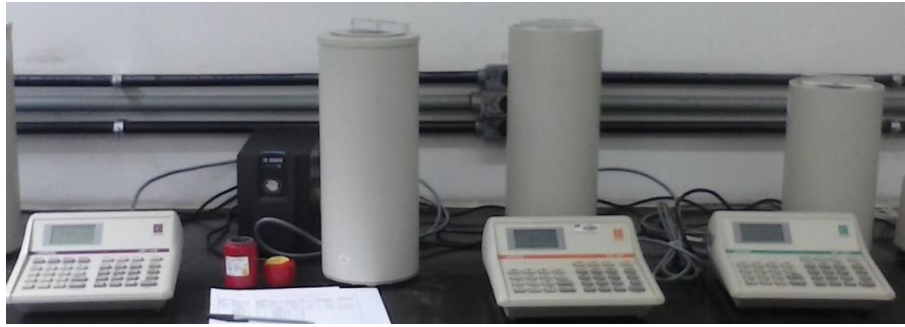


Figure 1: Example of an ionization chamber detectors, Capintec CRC 15W, CRC 15R and CRC 15BT.

The use of the radioactive sealed sources makes the process of checking the detector's accuracy easier; it is due to the fact that the production of these sources with more available materials and processes can facilitate the supply of the local demands. [2] These sources are prepared with radioisotope solutions of cobalt-57, barium-133 and cesium-137, with the final activity of 201.4 MBq, 9.7 MBq and 7.1 MBq (these values may vary), respectively, according to figure sources shown in Fig. 2.



Figure 2: Sealed radioactive sources produced with cobalt-57, barium-133 and cesium-137. Made at the Institute of Energy and Nuclear Research (IPEN).

These capsules and materials must be sturdy enough to prevent any radioactive material leakage under normal use. [3] After producing, the source must be visually examined to ensure its integrity and must also be approved in leakage test, performed according to the standard "International Standard Organization Radiation protection - leakage test methods" ISO 9978. [2]

1.1 Nuclear Medicine

A variety of radioactive sealed sources of different shapes, sizes and radioactivity levels are used for important applications in many fields. In nuclear medicine, they are commonly used in teletherapy and brachytherapy for the treatment of malignant diseases, bone density measurements, treatment of eye and prostate cancer, etc. [4]

Radioactive isotopes can be used to determine the target of compounds in the body. These studies begin with a compound that has a radioactive isotope as one of its constituent elements, the union of organic compounds and radioactive isotopes are known as radiotracers. [2] They are injected in patients and bound to tissues and bones according to their chemical affinity; the radioactivity generated by these radioisotopes is analyzed by a scintigraphic camera, generating two-dimensional or tomographic images.

The National Nuclear Energy Commission, CNEN, created the standard "Requirements for Radiation Protection and Security for Nuclear Medicine Services" CNEN-NE-6.10, which states that all nuclear medicine service must have standard reference sources of cobalt-57 and barium-133, for measuring their radiation detectors. [5]

1.2. Epoxi Matrix

Epoxides are ethers in rings of three members. The method used for their synthesis is the reaction of an alkene with an organic peroxide acidic, a process called epoxidation. [6] The process can be started simply with the addition of a catalyst such as an alkoxide or amine. [7] Solidified epoxy matrices in the glassy state have high compressive (500-700 kg/cm²) and adhesion strength (100 kg/cm²). Investigations of radiation resistance of some compounds, for example, have shown that the matrix remains unchanged with gamma radiation doses up to 10 000 Mrad, but has its elasticity increased and tensile fracture decreased with the radiation dose. No leakage was observed on sources produced with cesium-137 for a period of two years of testing. [8]

Epoxy resins are thermosetting materials readily converted through the curing reaction with a variety of chemical compounds (curing agent). Most resins are obtained from the condensation of epichlorohydrin (1-chloro-2,3-epoxy propane), and Bisphenol A [2,2-bis (4-hydroxyphenyl) propane], known as copolymers of diglycidyl ether bisphenol A or simply DGEBA. They have high interest to be employed in the manufacture of polymeric immobilization for radioactive material [8, 9], because:

- They are among the oldest resins of the epoxy class; they offer lower cost, availability and easy acquisition on the market.
- They have low toxicity and, consequently, low possibility of chemical contamination during handling.
- After the curing process it is obtained a polymeric material with high compressive and adhesion strength, [8] with a high radiation resistance, [10] as well as high resistance to thermal decomposition, which makes a material with high chemistry stability.
- Also originate, after curing, water-insoluble polymers, either in acid and alkaline environment, which guarantee any leakage or diffusion of the radioactive component. [8]

1.3. ISO Standards

To ensure compliance with the requirements of radiological protection, standards for the development and manufacture of sealed sources were established by the rules:

- "Radiation protection - sealed radioactive sources - General requirements and classification" ISO 2919. [12]

- "Radiation protection - sealed radioactive sources - leakage test methods" ISO 9978. [13] According to the standards, the sealed sources must be evaluated on several parameters. They must be classified by analyzing the toxicity of the radioisotope. Subsequently, tests must be performed to determine the performance of the product. These tests consist in exposing the sources to specific temperature, pressure, external vibration and puncture.

The approval in any of the tests will be determined by the ability of the sealed source to keep its sealing properties. After each test, the source must be visually examined for checking its integrity and must also be approved in leakage test, performed according to the standard "International Standard Organization Radiation protection - leakage test methods" ISO 9978. [2]

The leakage test can also be carried out by rubbing a fabric that can be moistened or not with water or ethanol. This tissue then has its activity examined. The activity must not exceed 185 Bq. [3, 11]

2. METHODOLOGY

The immobilization of radionuclides in sealed sources using matrices prepared with epoxy resin DGEBA stumbles into two problems:

- The miscibility of the epoxy resins with aqueous solutions. The sources of barium-133, cesium-137 and cobalt-57 are supplied commercially in acidic aqueous solutions. They are rarely supplied in the form of solid compounds. The epoxy resin and the aqueous solution are not easily miscible.
- When the aqueous solution is added to the resin, it decreases the mechanical and chemical resistance of the resin,

Both problems can be overcome. The miscibility issue can be minimized with emulsifiers and curing agents that are miscible in the epoxy resin. For the related loss of properties, especially the curing efficiency, it can be corrected by employing irradiation during the curing process. [14]

We used as basic formulation for the trials an rigid epoxy resin (diglycidyl ether of bisphenol-A) "DGEBA" Silaex SQ 2004, manufactured by Silaex Chemicals Ltd., viscosity 500 to 700 cps, epoxy equivalent weight 195-215 EEW and average density around 1.12 g/cm³. As curing agent, we used a modified polyamine catalyst base (diethylenetriamine) "DETA" SQ 3131 Silaex, the same manufacturer of the resin, with a viscosity around 3000 cPs and density 1.10 g/cm³. [15]

2.1. Curing Ability of Water-Containing Mixture at Room Temperature

The studies to test the ability of water solubilization were carried out using the mixture of epoxy (DGEBA) resin and polyamic catalyst (DETA), respectively, in the ratio of 100:20 parts by weight, in which were added varying amounts of an aqueous solution 0.1 M in HCl prepared in distilled water, and so make up 5, 10, 15 and 20% by weight of water in resin-catalyst mixture.

2.2. Acceleration of Epoxy DGEBA-DETA Curing

The curing process acceleration of the mixture epoxy resin (DGEBA) and the modified polyamic catalyst (DETA) was conducted in the Multipurpose Irradiator of Cobalt-60, situated at the Institute of Nuclear and Energetic Researches (IPEN) at doses of 20, 40, 60, 100, 150 and 200 kGy.

2.3. Tensile Test

The tensile strength tests according to ASTM D 680 [16], were made using 5kg load and a separation speed of 50 mm/min until rupture in an Instron Model 5567.

2.4. Thermogravimetric Analysis (TGA)

In TGA thermal tests, the equipment used was Model: SDT Q600, N₂ atmosphere and heating ramp of 10 °C / min. The sample was heated up to reach the 700 °C temperature.

The initial goals of thermogravimetric analysis was to investigate to what temperature the resin will begin to decompose and also the possible water evaporation during the temperature held for examining itself. This evaporation would be related to loss of radioactive material from the source, if any amount of water evaporated near the boiling point of water.

It was then investigated variation in mass of samples made with the formulations of the traction tests.

2.5. Manufacture of barium-133 source used in the verification of detectors

A source of barium-133 was produced for this work and further verification of the homogeneity of the radioactive material and leakage tests were performed.

The process of manufacturing this source, involves the immobilization of radionuclide in rigid epoxy resin and encapsulated in the standard geometry of scintillation flask of 25 mL, sealed with inert epoxy resin layer.

The source has produced the end a cylindrical radioactive volume of 21 ml (active element in epoxy resin, as shown in Fig. 3), density around 1 g/cm³, geometry and activities compatible to the demands of nuclear medicine procedures with regard to quality control and accuracy tests. In the case of source of barium-133, the quantity of radioactive solution represents less than 1% (50 µl) in the mixture of resin more catalyst (21 ml). The activity of the produced source of barium-133, was around 8,9 MBq.

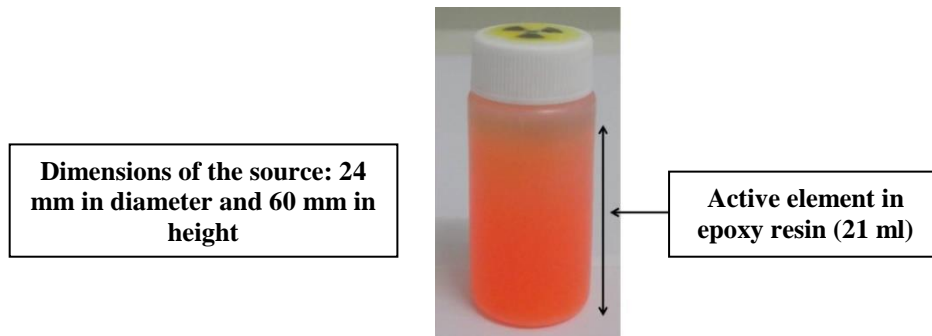


Figure 3 : Sources Barium-133, produced in this work.

2.6. Test of homogeneity of sources using the detectors of Capintec model

The analysis of the homogeneity of the distribution of the radioactive material in the final set was performed using three models of ionization chamber detectors, they were: Capintec CRC-15W, Capintec CRC-15R and Capintec CRC-15BT.

2.7. Execution of standardized leakage tests by the standard "International Standard Organization Radiation protection - leakage test methods" ISO 9978. [13]

For this work, were chosen the wipe tests and tests of immersion at room temperature and the hot liquid to 70 °C.

The source of barium was used for the test, the wipe was done with a piece of absorbent paper dampened with detergent Extran. The paper had its activity measure (before and after), to the measurements of the paper activities before and after the wipe, it was used ionization chamber detectors and sodium iodide (well type), both connected in Capintec CRC-15W model.

For Immersion test at room temperature (23 °C), the source was immersed in a beaker containing 250 mL of distilled water at 25 °C ± 5 °C for the immersion test at room temperature. The beaker with the sources remained in thermostatic bath for 24 hours. [13]

For the immersion in hot liquid to 70 °C, the source was immersed in a beaker containing 250 mL of distilled water at 70 °C ± 5 °C. The beaker with the source remained in bath for 30 minutes with simultaneous application of ultrasound during the entire period of immersion, as shown in Fig. 4. [13]



Figure 4 : Source immersed for leaking tests.

3. RESULTS

The addition of determined amounts of water to the epoxy resin-catalyst mixture does not affect the curing at room temperature. This curing process takes between 24 up to 48 hours, considering that the amount of water cannot exceed more than 20% of the epoxy system weight. Amounts above 20% lead to partially cured regions causing discontinued polymerization.

The tensile strength tests were conducted on pieces prepared with fixed amount of 100:20 parts by weight of epoxy resin and modified polyamic catalyst. The amounts of water, in form of an acid solution 0.1 M HCl, were added in portions ranging from 0 to 20% by weight of the resin-catalyst system, as shown in Fig. 5. The results revealed that there is a significant loss of the material's tensile strength.

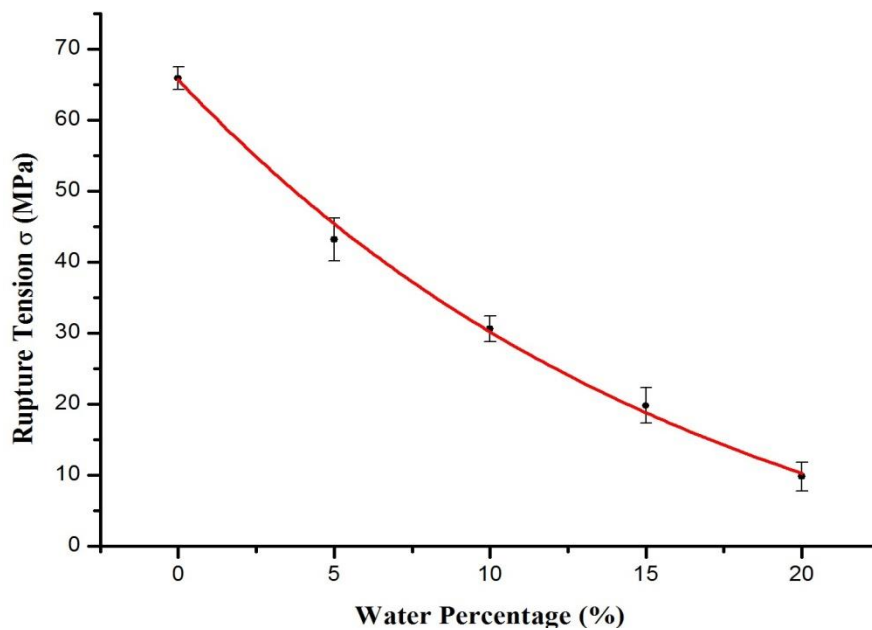


Figure 5- Rupture Tension *versus* Water Percentage.

The decrease of the material's resistance with water addition, can be explained by the loss of its plastic properties. It is due to a increased crystallinity that occurs in this process. The elongation of the material becomes constant from 5% of water addition, as shown in Fig. 6, in which it is represented the elongation of the pieces during the tensile test, depending on the percentage of water added to the catalyzed epoxy mix.

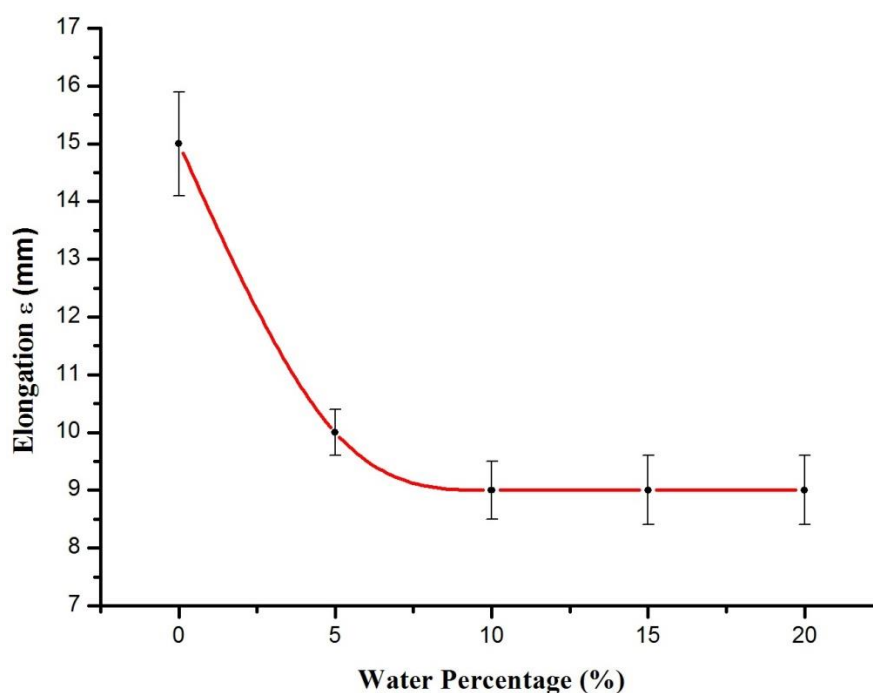


Figure 6: Elongation *versus* Water Percentage.

Tests to study how different doses of radiation can improve or not the material's properties were done. It was selected the same formulation using from the tensile test, but using the highest amount of water (0.1 M HCl) evaluated, 20% by weight. The dosages used were between 0 and 200 kGy.

After the tests, it was shown that irradiation enables increased strength in a dose around 33 kGy, then it was observed an inverse process, in which a reduction of the tensile strength until it reaches a level close to 150 kGy, where there seems to be a constant in tensile strength. However this tensile strength is higher than the initial state, when it was not used any dose, as shown in Fig.7.

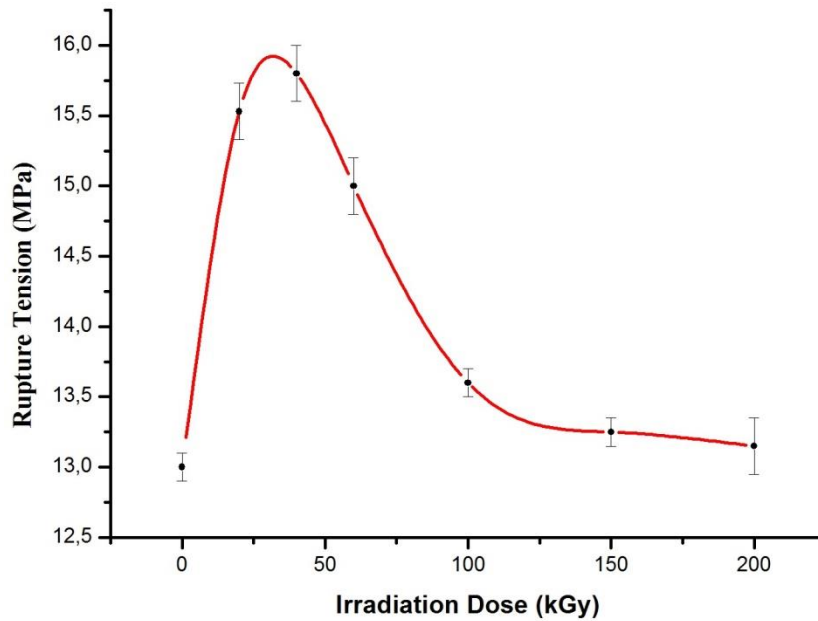


Figure 7: Rupture Tension *versus* Irradiation Dose.

The increased strength up to a dose of 33 kGy must be associated with the formation of additional cross-linking bonds in the polymerized material. On the other hand, the reduction of the resistance around 150 kGy must be due to the disruption of some cross-linking bonds. From 150 kGy, the threshold for the resistance, higher than the initial, but lower than doses around 33 kGy, is therefore associated with the stabilization on the bonds rupture.

The water added to the composition of the epoxy matrix is fully incorporated into the polymer structure since there was no significant change in density during irradiation, as shown in Fig 8.

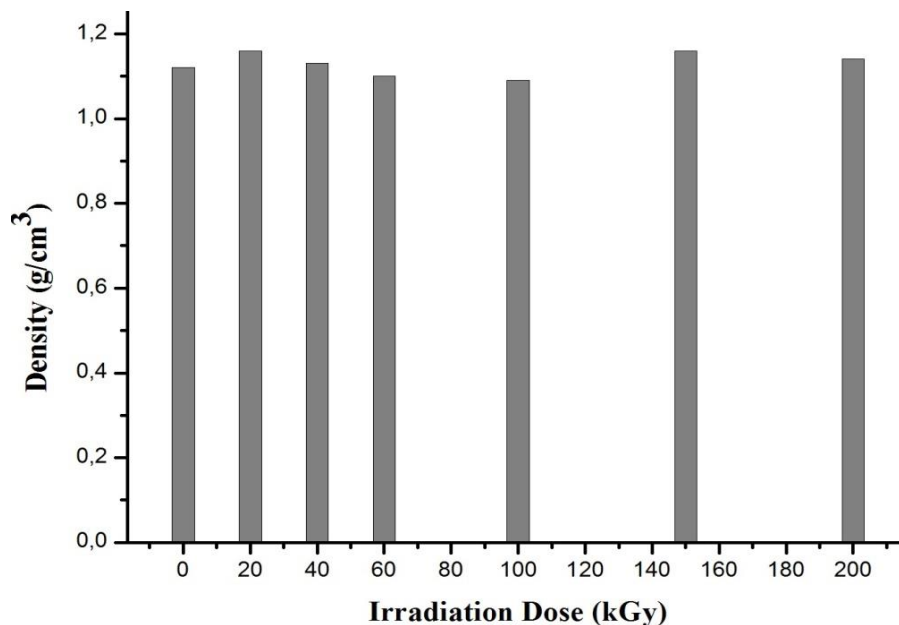


Figure 8: Density *versus* Dose.

In Figures 9 and 10 have the results of the thermogravimetric analysis. In Fig. 9, are shown the curves obtained in thermogravimetric analysis, we can see that the initial temperature of degradation for all samples showed practically the same value and the variations of mass close values.

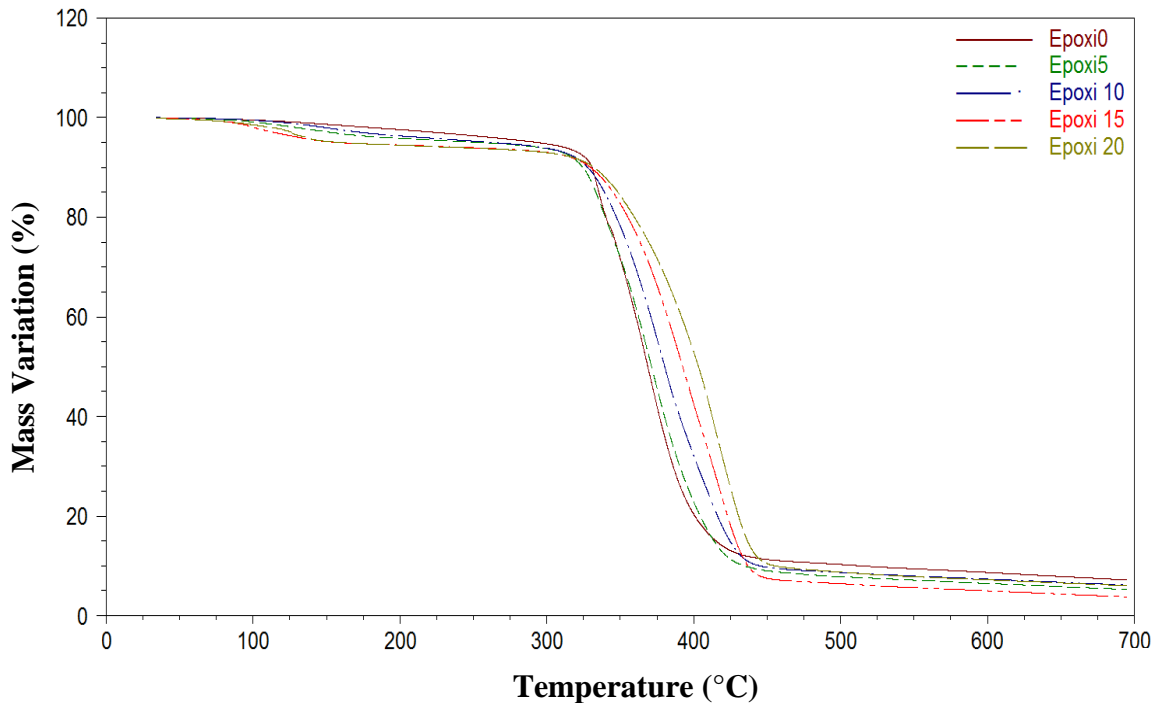


Figure 9: Mass variation in function temperature, for samples of percentage different of acid solution (0-20%) by weight of resin + catalyst.

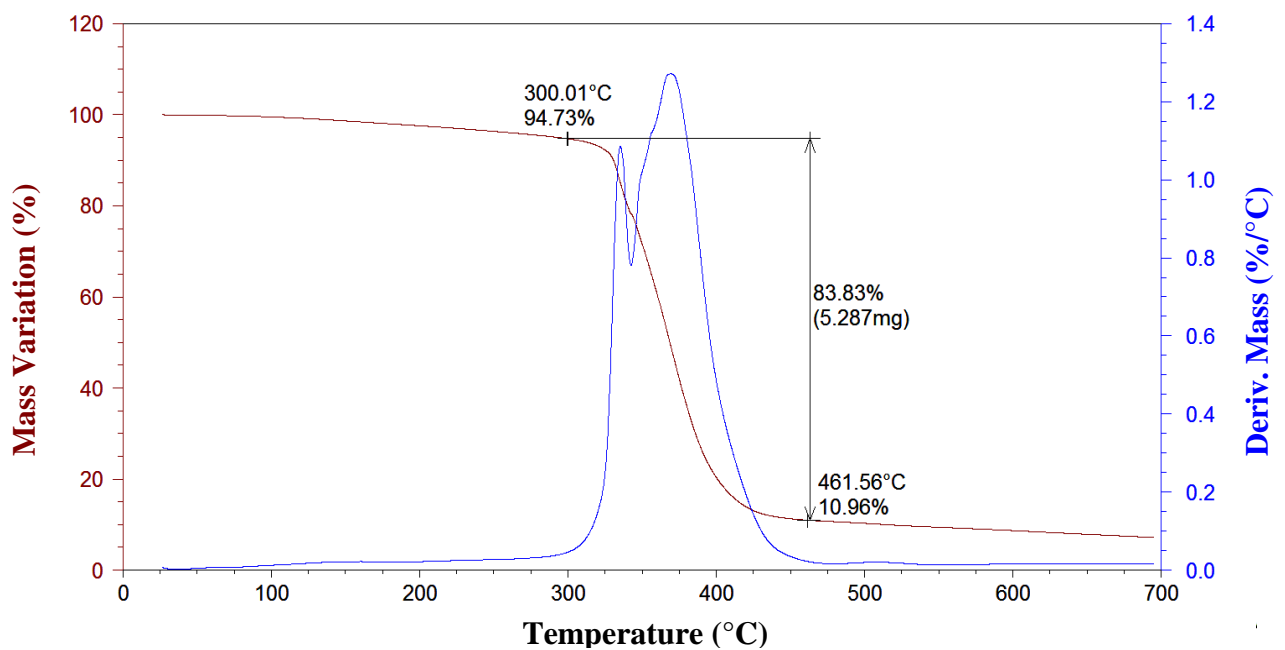


Figure 10: Mass Variation of pure resin + catalyst in function of temperature (sample without addition of the acidic solution).

There was no difference in proportion to concentrations of acid solution added to formulations. The added water is chemically bound to the matrix in all formulations and therefore shows the leaks the temperature rises to around 280 °C. Occurred only a small offset the final temperature of degradation.

It was noted also that the decomposition begins at a temperature around 300 °C, as is shown in Fig. 10, occurring a small displacement of this temperature depending on the concentration of an aqueous solution. Sources of verification under normal conditions does not reach that temperature, because they are stored at room temperature or refrigerated environment.

For analysis of the homogeneity of the distribution of the radioactive material, the data of the average of the values of the measurements obtained in the three detectors model capintec , are represented in the table 1.

Table 1 : Activity Measure of the source of barium-133 in three models Capintec detectors

Produced Source	¹³³ Ba		
	Capintec Detectors	15 R	15 W
Activity Measured (MBq)	8,91	8,91	8,85
Average of Activity Measured (MBq)	8,88		

The results obtained in the three detectors are quite significant, showing values very close.

In tables 2 and 3 are shown the results of the leakage tests of the source of Barium-133. The activities were measured in the ionization chamber and sodium iodide, both connected in Capintec 15W detector.

In table 2 is shown on the result wipe tests. In table 3 it is shown the result of the activity of the distilled water before and after the tests.

Table 2: Activity Measured of the paper used in the wipe tests (before and after)

Source	¹³³ Ba	
	Capintec 15W Detector	Ionization chamber
Activity (Bq) - Before	0	< 185
Activity (Bq) - After	0	< 185

In both detectors used (ionization chamber and sodium iodide), the activity measured on paper, after wipe, presented lower values to 185 Bq, required by ISO 9978, therefore the source is considered the leak proof.[13]

Table 3 : Activity Measured of the distilled water used in the immersion tests (before and after)

Source	¹³³ Ba	
	Ionization chamber	Sodium iodide (well type)
Activity (Bq) - Room Temperature	0	< 185
Activity (Bq) - Liquid hot at 70 °C	0	< 185

In both detectors ,sodium iodide and ionization chamber (connected in Capintec CRC-15W), the measured values of activity are far below that required by ISO 9978, in which the maximum of activity permitted in water used after soaking does not exceed 185 Bq, therefore, the source is considered the leak proof. [13]

4. CONCLUSIONS

Sealed sources can be made of DGEBA epoxy matrix and DETA polyamic modified catalyst, since the amount of radioactive material in the form of acidic solution does not exceed a content of 20 % by weight. The sources of verification do not reach this maximum quantity of radioactive solution, the greater quantity of radioactive solution is in the source of Cobalt-57 up to 5 % of the mixture in source produced.

The epoxy resin cure can be improved in relation to the cure at room temperature, with use of irradiation, since it is used a dose around 33 kGy during curing.

The water added to the epoxy matrix composition is fully incorporated into the polymer structure since there has been no significant change in density during irradiation and tests thermogravimetric analysis .

The results obtained from the three detectors for analysis of dispersion of the radioactive material, showed that the measurements are reproducible.

In the leakage tests, it was found that the sources are leak proof, the measurement of water activity used in the test showed a value below 185 Bq (according to International Standard Organization- Radiation protection – sealed radioactive sources - ISO 9978 Standard), proving the efficiency of rigid epoxy resin as material to seal the radioactive material, classifying the source produced in this work as a sealed radioactive source.

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