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MATERIAL TESTING – A GLIMPSE TO OPPORTUNITY

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Abstract: *Innovation in the field of material development increased continuously in the last decade and this trend tends to, at least, to maintain at this level. Innovation is also supported by national (UEFISCDI and ANCSI) and international (Horizon 2020) programs and competitions of research projects. The need for new, complex, dedicated etc. materials is a request that comes from both manufacturers who want to overcome their competitors, gain a larger market share and sometimes seize new markets but also from the consumers who require dedicated materials for their application and based on that, deliver more reliable, cheaper and competitive products. The most dynamic markets regarding new materials are the automotive, aerospace and nuclear industries. Material testing represents the only way to know and understand how materials will behave in certain or in various situations or operations. Information gathered and analysed from material characterization helps in reaching all the purposes mentioned above from both perspectives – manufacturers and customers. The objective of this paper is to underline the general importance of material characterization. Also, it identifies the opportunities of knowing the proprieties of materials for better usage, calculating the working lifetime, reducing costs etc. The case study describes how analytical and comparative analyses are carried out, in order to show the behaviour of the seals.*

Keywords*: pneumatic seals, ionizing radiation, FTIR, Raman, TG/DSC*

1. Introduction

In today manufacturing market, there is a real and aggressive competitiveness increased by the financial crisis. In search for profit and sometimes for survival, companies change their market strategies and approaches, production, policies, objectives, diversify products etc. in order to maintain their market share at least, if not to increase it. Innovation in the field of material development increased continuously in the last decade and this trend tends to, at least, to maintain at this level. Innovation is intensively supported by national (UEFISCDI and ANCSI) and international (Horizon 2020) programs and competitions of research projects. These project calls offer non-refundable funding either for join programs between SMEs and research institutes and universities or single participant program. Also, there are project calls which finance the construction of laboratories and acquisition of research and testing equipment. These programs give access to non-refundable funds to sustain research in new material development.

The need for new, complex, dedicated etc. materials is a request that comes from both manufacturers who want to overcome their competitors, gain a larger market share and sometimes seize new markets but also from the consumers who require dedicated materials for their application and based on that, deliver more reliable, cheaper and competitive products. The most dynamic markets regarding new materials are the automotive, aerospace and nuclear industries.

Material testing represents the only way to know and understand how materials will behave in a certain/various situations or operations. Information gathered and analysed from material characterization helps in reaching all the purposes mentioned above from both perspectives – manufacturers and customers. So, the basic reason for material testing is to evaluate its behaviour under the requested conditions. Material testing is regulated by numerous standards, national e.g. RO ISO, DIN ISO, ASTM, AFNOR ISO etc. and international, ISO, regardless of testing type and third party organizations. In most cases, choosing a testing standard is easy and it is based on what characteristic is investigated. This basically requires a standard material which is used in standard applications. The problem appears when neither or one of the test and material are not standard. This is the case of typical new materials and/or applications. For example, in nuclear

industry there is a constant research of new materials that will resist to high radiation doses and maintain their basic functionalities, especially in nuclear facilities and radioactive waste management. The list continues when an atypical process is used for existing materials e.g. the preservation of cultural heritage (leather, textile, paper materials) that are treated with gamma radiation in order to be decontaminated of fungi, bacteria, mould etc. In this case, there is no standard that characterize the behaviour of these materials under the effect of ionizing radiation.
Under these aspects material testing gains an important and indispensable role in day to day activities helping material science to further develop.

2. The role of material testing

In order to manufacture a product there is the need to select the material or mix of materials needed. The selected composition will be processed in order to obtain the final product. Because of this process which implies material processing, it is imperative to analyse the input characteristics against the final output. For example, in a basic plastic material, the base polymer is mixed with various amounts of anti-oxidants, processing aids, plasticizers etc. [1]. This final mix plus the production technology influences greatly the behavioural characteristics of the final product. Taking into account that manufacturers use their own technologies, the final products have different characteristics in service even if they are manufactured under the same ISO. This is one reason for testing, establishing the final characteristics and identify the differences between two similar materials. The results help in choosing the optimum product/material for a given process.
Evaluation of material characteristics depends on the type of the test that is conducted. That is why is very important to know from the start that the results are relevant to the material application and usage. In practice this is called test method validation which is the documented process of ensuring a test method is suitable for its intended use [2]. It involves establishing the performance characteristics and limitations of a method and the identification of influences which may change those characteristics [2].
Beside selection of tests, there is always the question if the chosen test is in fact the right one. For example, it is important that a material will withstand a particular load so a loading test will be conducted in order to evaluate its resistance to a loading force according to a designated standard. Identification of the optimum test is vital for the correct choosing of materials. In this way, only the needed characteristics will be evaluated for material behaviour.
Material characterization implies the use of numerous tests from different categories: chemical, electrical, structural, thermal analysis, surface characterization etc. There are also mechanical (strain, elongation, stress etc.) and analytical (FTIR, ICPMS, XRF, SEM, RAMAN etc.) tests, both destructive and non-destructive. When the material or product plays an important role in process, it is recommended that the initial test to be validated by a complementary one, in order to obtain accurate interpretation of results. This approach is supported by the fact that failure in process can determine either stopping of the manufacturing line or worst, production of non-conform products. These accidents imply high costs, especially in domains that rely on big and continuous production size. This is another reason to material testing, thus confirming and supporting the results, if possible, through another type of test.
Regardless of the information given by the material or product manufacturer, material testing should be conducted in order to take into consideration the particularities of the production conditions like dust, moisture, temperature etc. Also, temporary conditions like working in high temperature should be taken into consideration thus testing the materials as close to the real environment. Although it is rather difficult to simulate the exact condition of process, a much easier approach is to conduct failure analysis and establish the critical parameters that will break down the material.
Sometimes, a simple material testing can be used to determine if the product has changed some of its generic characteristics. Take for instance, the case when a customer has a long time products provider. Even if the product is basically the same, due to some changes in providers'

technological process and mix of materials, it can result in different and important material characteristics and behaviour.
In conclusion, materials need to be tested, in general, in order to predict their behaviour under given circumstances and in particular for research and development purposes.

3. Case study: analytical tests for piston seals

The tests have two objectives: first is material identification and second is material characterisation before and after irradiation.
The tests were conducted on a Bruker FT-IR spectrometer, Vertex 70 class equipped with: FT-ATR Platinum module, spectral dominium 4500-500 cm^{-1} and spectral resolution of 4 cm^{-1} and Raman module, RAM II for non-distructive analysis, power 1 ÷ 500 mW, resolution 1mW, spectral domenium 4500-500 cm^{-1}, spectral resolution 4 cm^{-1} and 64 scans.

1. Material identification: was done using FT-IR Spectroscopy – ATR (Attenuated Total Reflectance) and RAMAN spectroscopy analytical techniques. This type of compound is a linear co-polymer, alternatively divided in “hard” and “soft” segments. “Hard” segments are rigid molecules with high polarity while “soft” segments are flexible molecules and low polarity [3].

In figure 1 it is shown the spectrum of the seal (in black color) and the specter of polyurethane (in blue color) from Bruker polymer data base. The appropriate shape of bands indicates the material as being thermoplastic polyurethane (TPU). The small differences are caused by the particular recipe of the seal. In addition, the spectrums were verified against literature results. FT-ATR spectrums identified bands characteristic to polyurethane, through functional groups and its vibrational modes (stretch vibration N-H at 3331 cm^{-1}, stretch vibration C=O at 1729 cm^{-1} and at 1704 cm^{-1}) [4], [5], [6]. Also, the presence of bands at 1597 cm^{-1} and 1414 cm^{-1} stretching vibration which are characteristic to aromatic rings, probably from chromophore, indicate polyurethane [7].
Another band from the ATR spectra which indicates the presence of urethane group is attributed to stretch vibration C-N (amid II band) and vibration of deformation N-H) and found at 1531 cm^{-1} [8].

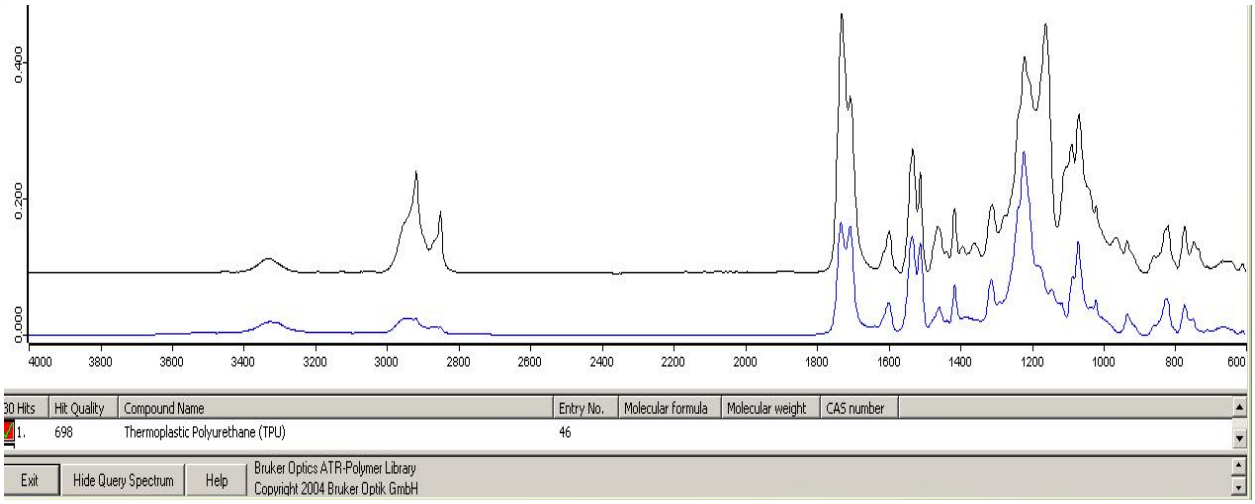

Fig. 1. Analysed seal spectrum (black) and TPU data base spectrum (blue)

The seal’s FT-Raman spectrum is shown in figure 2. Identification of polyurethane characteristics bands were made using speciality literature. There were identified the following polyurethane characteristics: stretch vibration of =C-H from the aromatic cycle at 3065 cm^{-1} and deformation vibration at 1184 cm^{-1} [8]. Symmetric and asymmetric stretch vibration of C-H from $–CH_2$ is present at 2917 cm^{-1} and 2871 cm^{-1} [8]. Also bands characteristic to stretch vibration of C=) from ester and urethane at 1731 cm^{-1} [9]. The presence of aromatic cycle is observed at 1615 cm^{-1} through stretch vibration of C=C [9], [10]. Deformation combined vibrations of N-H grouping and stretch vibration C-N (amid II band) are assigned to band 1536 cm^{-1} [8], [10]. Urethane grouping from amid band IV appears around band 1255 cm^{-1} through coupled vibrations C-N/C-O [7].

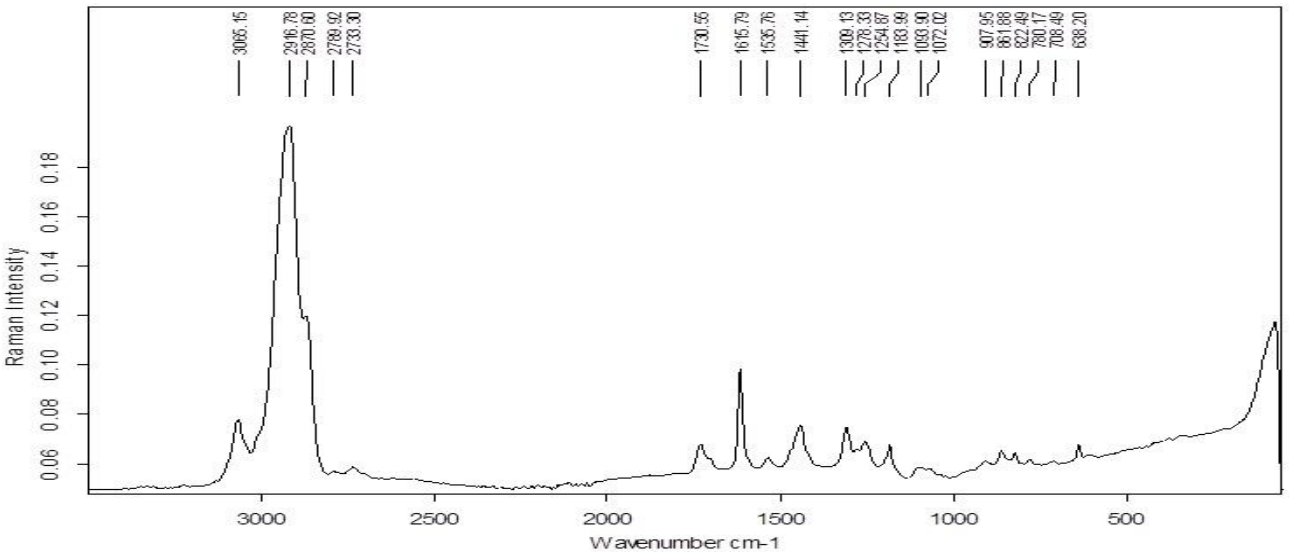

Fig. 2. FT-Raman spectrum

2. Material characterisation before and after irradiation. There were used three analytical techniques: FT-ATR, TGA (thermogravimetric analysis) and DSC (differencial scanning calorimetry).

The seal was irradiated at a dose rate of 1 kGy/h to 1.5 kGy/h. The total dose received is around 3000 kGy. Polyurethane has a tolerance level to radiation of 10000 kGy [11]. The exact value of dose rate and total dose is not relevant in this case because the purpose of this study is to show how analytical and comparative analysis are carried out.

In figure 3 a) it is shown the non-irradiated seal and in fig. 3 b) the irradiated seal. The visual effect of radiation is the change in colour from green to brown.

Fig. 3. (a) non-irradiated seal

Fig. 3. (b) irradiated seal

Spectroscopy analysis using FT-ATR and Raman are complementary tehniques. Infra-red spectrums offer important information about the vibrations which accompanies the molecule dipol momentum changes. FTIR spectrum contains information regarding the presence of functional grouping/types of molecular bonds. Raman spectrums offer information about vibrations accompanied by the modification of molecular polarisability. Vibrations from the IR spectrum are usualy weak in Raman spectrum and strong in FTIR spectrum. From the qualitative point of view, asymetric vibration modes have proeminent bands in IR due to polar bonding O-H and C=O while in Raman spectrum appear vibrations involved in simetrical bonds, C=C and C-C.

FT-ATR technique was also used for comparison the spectrums of non-irradiated (in black color) and irradiated (in blue color) seals (fig. 4).

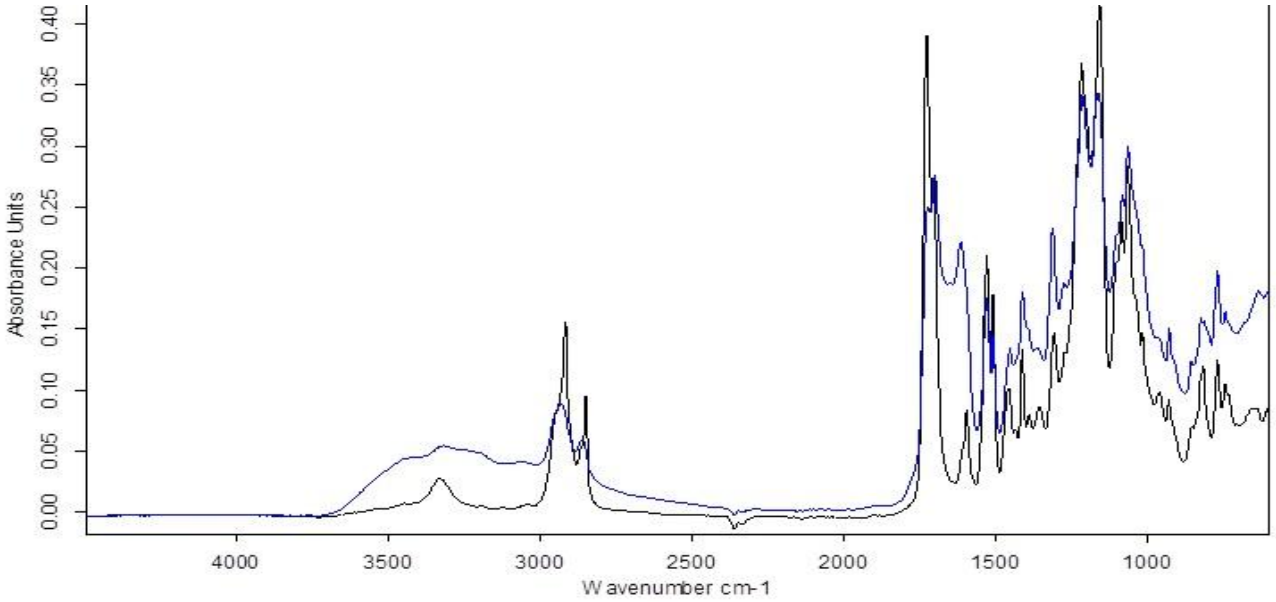

Fig. 4. FT-ATR spectrum comparison between non-irradiated seal (black) and irradiated seal (blue)

An important difference is the disappearance of band peak 1597 (present at the non-irradiated seal) from the spectrum of the irradiated seal (fig. 5) which is characteristic to C=C grouping from the aromatic cycle, indicating chemical changes and degradation of aromatic structure [4].

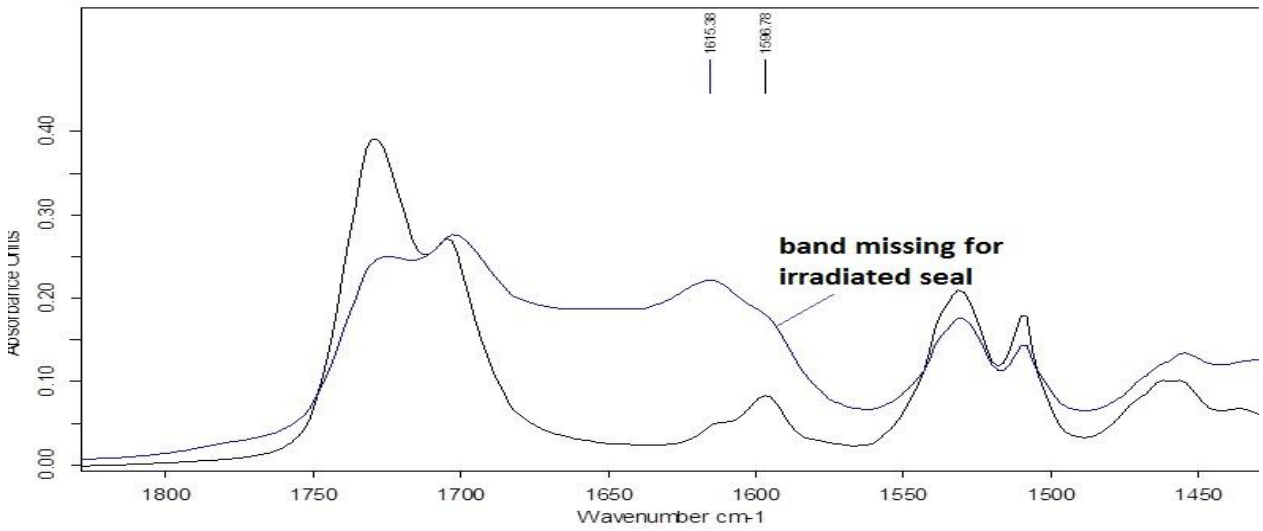

Fig. 5. FT-ATR spectrums overlay showing band 1597 cm^{-1} missing from the irradiated seal

For the irradiated seal, in the interval between 2950 cm^{-1} and 2850 cm^{-1} it can be observed a decrease in band intensity, indicating a degradation of C-H grouping. Also, the decrease in intensity (absorbance) of band 1729 cm^{-1}, from 0, 39 to 0,24 (fig. 6 and fig. 7), can be explained by the decomposition of the structure of aliphatic esters [5].
The irradiated spectrum has larger bands in the 3500-3000 cm^{-1} area and 1800-1550 cm^{-1} area indicating effect of radiation [12], [13].

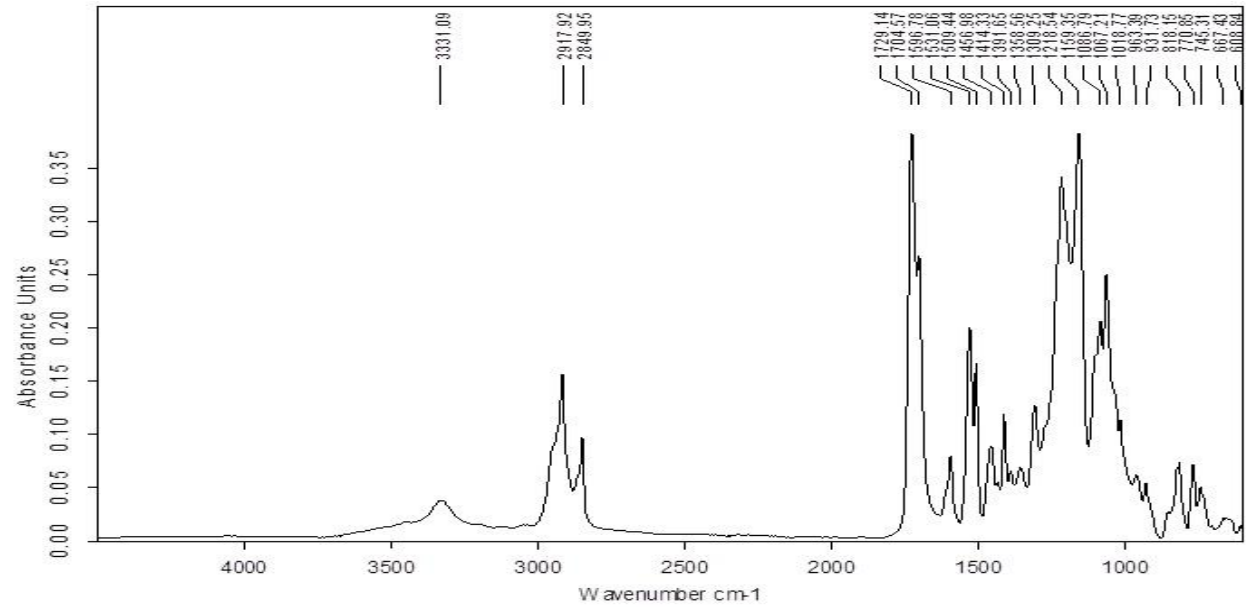

Fig. 6. FT-ATR spectrum for non-irradiated seal

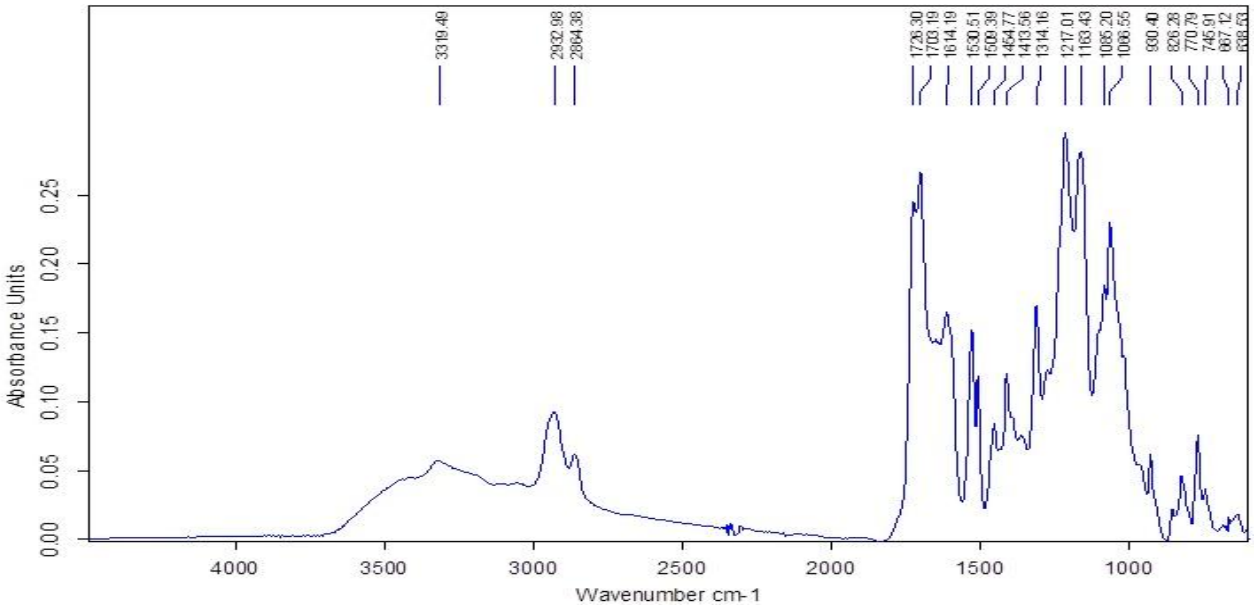

Fig. 7. FT-ATR spectrum for irradiated seal

The thermal simultaneous analysis TGA/DSC tests were carried out on Nietzsche Geratebau STA 409 PC Luxx. The analysis took place in an inert nitrogen atmosphere with constant temperature rising of 10 K/min, from 20^{0}C to 590^{0}C and 100 ml/min gas flow.
From both seals thermograms (fig. 8) there are three decomposition stages, correlated with seals' composition. For the non-irradiated seal, degradation starts at approximately 317^{0}C with decomposition at 330^{0}C and mass loss of 7%, meaning that volatile compounds were created as a result of "hard" segments decomposition [3]. The next stage is represented by the most mass loss of ~74% at 413^{0}C, being included depolymerisation and low polarity segment division [3], [14]. Complete decomposition finalises at 468^{0}C.

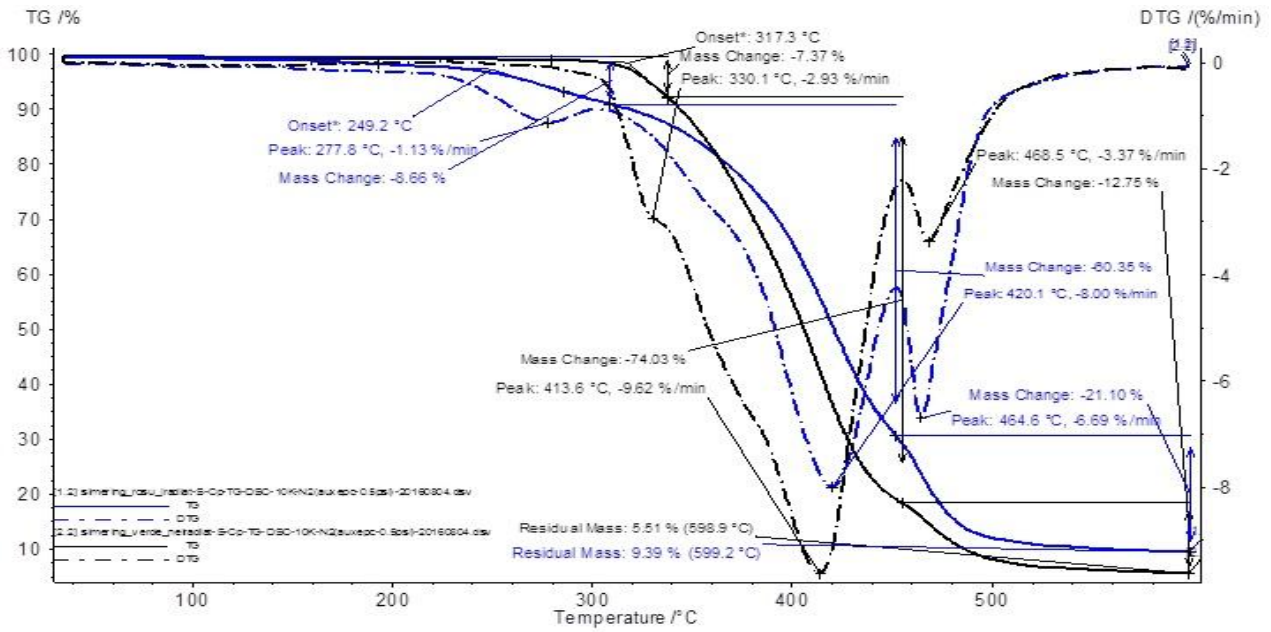

Fig. 8. Overlay TG/DSC curbs for non-irradiated seal (black) and irradiated seal (blue)

For the irradiated seal, degradation starts earlier at 249^{0}C with decomposition at 278^{0}C and mass loss of ~9%. In literature it is reported an interval between 250^{0}C and 320^{0}C corresponding to "hard" segments decomposition [3]. Second and third stages present maximum temperatures of 420^{0}C and 464^{0}C being attributed to "soft" segments like polyester, which decomposition temperature is above 400^{0}C [15], [16], [17]. The effects of radiation refer to an earlier scission of molecular chains from "soft" and "hard" segments [18].
Thermal stability depends on chemical composition, chain length, the symmetry and distribution of segments molecular weight [19].

4. Conclusions

Material testing is a very useful tool in evaluating the behaviour of materials and products. Its results can and should be used for continuous assessment of manufacturing quality, improvement, client satisfaction, innovation etc. These are the basis of choosing, changing, improving, innovate etc. products and materials. Nevertheless, new materials can determine and support new applications and even new working fields. A lot of work and knowledge is given to improve and build new and higher performance testing machines and methods in order to evaluate more quickly and accurate characteristics of materials. But these improvements come with a price. It is very important to know how to choose the relevant tests, complementary tests, standards, machines in order to correctly evaluate the material characteristics. The analyst must continuous evaluate and research the best solutions (standards, methods, machines, literature etc.) in order to give a relevant result and answer the exact question. In addition, the simulation environment should be as close as to real working one.
The case study described a routine material identification request and an inter-comparison between two seals, one being new and one being subjected to ionizing radiation. In this case, the exact value of dose rate and total dose are not relevant because the purpose of this study is to describe how analytical and comparative analyses are carried out. The chosen techniques showed to be relevant and useful, highlighting the characteristics of both seals. Nevertheless, it showed the importance of researching through technical and scientific literature in order to evaluate the results.

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