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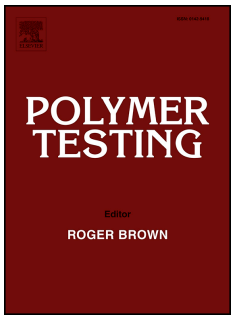

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Material Properties

MECHANICAL BEHAVIOR AND MICROSTRUCTURAL CHANGES IN POLYURETHANE EXPOSED TO HIGH DOSES OF X RAYS, GAMMA RAYS OR NEUTRON IRRADIATION

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ABSTRACT

Polymeric materials are widely used in applications where the environmental conditions entail their exposure to different sources of irradiation (in most cases ultraviolet or low dose of electromagnetic irradiation for sterilization). In contrast, in this study we have assessed the modifications undergone by a series of polyurethane joints exposed to high radioactive doses of either X-rays or gamma rays (with doses of 20.5, 100, 300 and 900 kGy) or neutron irradiation (with a fluence of $7.23 \cdot 10^{10}$ n / cm^2) which are typical of the environment of nuclear reactors. Tensile tests were carried out to assess the change in mechanical properties derived from the radioactive exposure. Three mechanical parameters were used to monitor the evolution of strength, ductility and toughness: the tensile strength (σ_{max}), the strain corresponding to σ_{max} ($\varepsilon_{\sigma max}$) and the density of energy absorbed prior to maximum load ($U_{\sigma max}$). With regards to X and gamma rays, a negative impact of radiation on strength, ductility and toughness was observed. The detailed statistical analysis of the results has shown that a threshold dose of 300 kGy must be overcome to trigger the damage process. For the fluence employed in this study, neutron irradiation produced very little change in the mechanical properties. The SEM fractographic study has allowed the influence of irradiation on the material failure mechanisms to be identified. Thus, the fracture surface of unirradiated samples shows evidence of plastic deformation and ductile tearing. In contrast, the fracture surface of those samples exposed to a dose of 900 kGy corresponds to brittle fracture. In a consistent way, samples exposed to neutron irradiation have a fracture surface similar to that of the non-irradiated material. In summary, electromagnetic radiation for doses above the threshold leads to the embrittlement of polyurethane.

Raman spectroscopy was employed to identify the microstructural changes induced by the different sources of radiation at the molecular level. The band corresponding to the vibration of the C-H bending bonds present in the polyurethane was measured as a function of the dose, finding a strong correlation between its vibration frequency and the dose of exposure to electromagnetic radiation. This shift is more sensitive than the mechanical material response since the frequency is affected at doses of 100 kGy, below the threshold previously identified for any of the mechanical properties. This correlation opens the door for the use of Raman spectroscopy as a novel non-destructive tool to characterize the microstructural effect of irradiation on polyurethane.

KEYWORDS: Polyurethane; high dose irradiation; mechanical properties; fractography; Raman spectroscopy.

1. INTRODUCTION AND AIM

Radiation may degrade the mechanical properties of materials so that they are no longer mechanically suitable. This is of particular concern in the environment of nuclear reactors where the materials are usually exposed to a variety of sources of radiation including X rays, gamma rays and neutrons. The effects of radiation on concrete and metals have been extensively studied, due to their relevance for the structural integrity of components in nuclear facilities. [1]. Polymeric materials are increasingly used for technological applications under irradiation environmental conditions. In addition, radiation-processing has the potential to play an expanding role in polymer manufacturing since ionizing radiation is a powerful means of modifying polymers. For

these reasons, describing, quantifying and understanding the effects derived from exposing polymers to ionizing radiations is becoming increasingly important. For instance, polymers are used as insulators, cable systems or packing materials in nuclear plants and high intensity proton accelerators [2]. In addition, polymer-based medical devices are commonly sterilized by means of gamma rays and electron-beam irradiation.

The ability to predict lifetimes when materials are irradiated is still a limiting factor in a number of existing radiation technologies [3]. Even although polymeric materials generally possess a lower structural responsibility in nuclear facilities, there is no doubt that their possible deterioration by radiation can lead to undesirable situations from the logistic and economic viewpoints. Thus, as stressed by Cassidy et al. [4], "Degradation mechanisms in polymers due to gamma irradiation also impact the reliability of instrumentation and power cable systems necessary to maintain safe operation and extend the lifetimes of Light Water Reactors (LWRs) for nuclear power".

Polymers may exhibit a wide range of radiation effects; the formation or rupture of chemical bonds usually results in irreversible effects changing the chemical, thermal or mechanical properties of the material. The reactions undergone by irradiated polymers can be broadly grouped in two types, namely, cross-linking and chain scission. The cross-linking results in the formation of new chemical bonds between polymer molecules while chain scission implies the fracture of polymer molecules. In general, cross-linking improves the strength of the polymer materials whereas the opposite occurs under chain scission. However, the degree and direction of the change is extremely material-sensitive.

There are currently few publications on the changes in properties of polymers exposed to high radioactive doses. As noted above, this is because this type of material is not

commonly used in environments as hostile as nuclear reactors. In contrast, numerous studies have been carried out in which the influence of ultraviolet radiation on various properties of different polymers is analyzed, such as [5][6][7][8]. The present study assesses the influence of high doses of X rays, gamma rays and neutron irradiation on the mechanical properties of the polyurethane constitutive material of a series of junctions that are part of pneumatic clamping modules. These modules are employed under very adverse conditions, in contact with metallic materials previously exposed to high doses of radiation (spent fuel rods, for instance). In this study, the strength, ductility and toughness of polyurethane were determined by means of quasi-static tensile tests on unirradiated samples and on specimens exposed to electromagnetic radiation with doses of 20.5, 100, 300 and 900 kGy or to neutron irradiation with a fluence of $7.23 \cdot 10^{10}$ n / cm^2. These doses are typical of the environment of nuclear reactors. To the best of these authors' knowledge, there are no previous works in the scientific literature in which the consequences of exposure to high radioactive doses on the mechanical properties of polyurethane are addressed.

A review of the specialized literature allows two main groups of studies related to the exposure of polyurethane to radioactive sources to be distinguished. On the one hand, works in which the polyurethane was exposed to ultraviolet radiation to assess the changes undergone by different properties (microstructural, thermal, mechanical, etc.). Within this first group, there is a small number of studies focused on the mechanical properties. For instance, Boubakri et al. [9] studied the changes in appearance and morphology, thermal properties and mechanical properties of thermoplastic polyurethane exposed to ultraviolet rays (through accelerated aging). According to their results, there was competition between chain scission and crosslinking mechanisms.

Thus, the Young's modulus and the stress at a strain of 200% initially decreased and then increased progressively, revealing an increase in crosslink density.

There are also a number of contributions in which the polyurethane is sterilized by exposure to electromagnetic radiation. For instance, Gorna and Gogolewski [10] exposed different biodegradable medical polyurethanes (with varying hydrophilic-to-hydrophobic segment ratios) to gamma radiation at a dose of 25 kGy (which is the standard dose for sterilization). They found that the mechanical degradation is strongly material-sensitive. Thus, the decrease of tensile strength was 12% for the more hydrophobic polyurethanes and 50% for the more hydrophilic polyurethanes. Abraham et al. [11] studied the changes in mechanical behavior induced by sterilization through gamma irradiation on two commercial medical-grade segmented polyurethanes (Biospan^{TM} and Chronoflex^{TM}). They obtained the stress–strain curves of these materials before irradiation and after being exposed to doses of 37.6 and 61.6 kGy, respectively. None of these materials showed significant changes in the secant moduli at 50% elongation or in the elongation at failure.

Within this context, one of the main novelties of our work lies in the doses to which the polyurethane has been exposed (reaching 900 kGy for gamma rays and a fluence of $7.23 \cdot 10^{10}$ n / cm^2 for neutron irradiation). The thorough statistical study carried out has allowed the influence of radioactive exposure and mechanical properties to be properly addressed, identifying the threshold that must be overcome to trigger the mechanical damage in this material. The relation between failure micromechanisms and the type and amount of radiation was elucidated through a fractographic study. Finally, Raman spectroscopy was employed to determine the microscopic changes in the material after being exposed to irradiation. As a result of the present work, we have identified the modifications of the mechanical behavior of the material derived from the exposure to

the radioactive environment and these changes have been correlated with the micromechanisms developed in the polyurethane. The findings derived from the study by Raman spectroscopy have made it possible to develop a novel non-destructive method to monitor the damage undergone by the material which could prove extremely valuable in carrying out on-site inspections regarding the level of accumulated damage in polyurethane from exposure to radioactive sources.

2. MATERIAL

The pneumatic clamping modules consist of a fixed metal part that carries the pneumatic drive input coupled to a polyurethane joint, which is actioned by pressurized air (6-7 bar) making the joint press on the part to be held or lifted. Specifically, this type of clamping module is employed to hold metallic rings in nuclear facilities (nuclear fuel rods, for instance). The typical irradiation conditions are a dose of 100-200 Gy/h and a flux of 10^4-10^5 n/cm^2/s. Fig. 1 (a) shows a diagram of a tube-holding element consisting of three clamping modules while Fig. 1 (b) presents a photograph of one of the modules. The lower part (grey) corresponds to the metal casing and the upper part (black) to the polymeric joint.

Figure 1. (a) Sketch of a hexagonal tube-holding part consisting of three clamping modules. (b) Photograph of one of the modules.

A total of 60 polyurethane joints were available for this study. They were subjected to either X and gamma rays at different doses or neutron irradiation. Fig. 2 shows a picture with several samples while Table 1 summarizes the experimental groups involved in the research. It is worth noting that the experimental part was conducted under single blind conditions, that is to say, the designer of the research was in full possession of the

information but the experimenter (in charge of carrying out the tensile tests, the fractographic or Raman studies) did not know the origin of the samples or the group they belonged to. This measure was applied to avoid skewing the results (which is of particular relevance for the fractographic study, based on visual inspection of the samples).

The density (ρ) and hardness shore D (H_{SD}) [12] of the samples were measured in the as-received condition obtaining the following results: $\rho = 1.22 \pm 0.03$ g/cm^3, $H_{SD} = 29.6 \pm 0.6$.

Figure 2. Photograph allowing some of the samples available for the study to be appreciated, as well as their dimensions (in cm, see the ruler).

Table 1. Classification of the samples.

Number of the sample	Dose (kGy)
51 a 60	0 (Control group)
31 a 34	20.5
01 a 10	100.0
11 a 20	300.0
21 a 30	900.0
35-40	Neutrons

3. EXPERIMENTAL AND ANALYTICAL METHODS

3.1.- Chemistry

The chemical composition of the samples was determined using Fourier Transform Infrared (FT-IR) spectroscopy. A NICOLET^{TM} model NEXUS with a resolution of 2 cm^{-1} and a spectral range of analysis between 400 and 7000 cm^{-1} was used. Thermogravimetric analysis (TGA) was employed to measure the amount of polymer,

black carbon and inorganic residuals in the material using a SETARAM™, model SETSYS EVOLUTION. For the TGA, the samples were subjected to two heating cycles. First, they were heated from room temperature to 600ºC in a nitrogen atmosphere to determine the polymer content through its decomposition; next, in a second heating from 600ºC to 900ºC, the amount of black carbon was obtained by combustion.

3.2.- Irradiation of the samples

The polyurethane joints were irradiated with either X rays, gamma rays or neutron radiation. The X-rays were applied by means of an X-rays source (YXLON™, Model SMART 200E) which provides a dose of 1.02 Gy / min at a distance of 25 cm from the origin of the X-ray beam, with a voltage and intensity of 200 kV and 4.5 mA, respectively. The energy of the photons makes up a continuous spectrum up to 200 keV. This device is equipped with a cooling system that allows intervals of irradiation of 80 minutes. The NÁYADE Unit of Irradiation at CIEMAT was employed for the gamma-rays irradiation of the samples. This Co-60 source emits gamma rays between 1.17 y 1.33 MeV. The current activity of the Unit is 15 kCi, distributed among 60 sources. The device G-III belonging to this facility was employed, which consists of 12 active sources distributed in a semicircular arrangement providing a dose of 1780 kGy/h. The Am-Be source used for the neutron irradiation of the samples has an 241-Am alpha activity of 3Ci, and the total neutron intensity is $\Phi_n = 6.6 \times 10^6$ neutrons/s ± 10% (in geometry 4π). The energy spectrum of the source extends to 10 MeV. The source is placed in a paraffin container, where the thermal neutron flux at a distance of 5 cm is between 2 and 2.5 10^4 n/cm$^2 \cdot$s.

3.3.- Tensile tests

Due to the complex geometry of the elastic junctions, see Fig. 2, it was necessary to manipulate them in order to extract tensile specimens of suitable geometry. As shown in Fig. 3(a), firstly, each sample was opened separating the central region and the perimeter. In order to extract the specimens from the previously separated perimeter region, a steel die was manufactured, see Fig. 3(b); this is endowed with a sharp edge corresponding to the shape of the tensile specimen. The specimens consist of a central shaft of smaller cross-section, and two ends with a larger surface, in order to achieve the maximum friction between them and the clamps of the testing machine (reducing in this way the possibility of sliding during the test). Finally, Fig. 3(c) shows a photograph of one of the specimens manufactured following this procedure.

Figure 3. Description of the process developed to manufacture the tensile specimens from the polyurethane joints.

The tensile tests were carried out until fracture, using a servo-mechanical ME-405 (Servosis™, Spain) universal testing machine, equipped with a load cell of 125 N. Following the protocol described in ISO 527 [13], the tests were performed under control of displacement conditions, at a crosshead speed of 1 mm/min, at room temperature. The applied load and the elongation of the specimens were continuously recorded. Then, employing the initial gauge length and the cross-section of each specimen, the stress-strain curves (engineering variables, σ-ε) were obtained.

The strength, ductility and toughness of the material were assessed, respectively, through the tensile strength (σ_{max}), the strain corresponding to σ_{max} ($\varepsilon_{\sigma max}$) and the density of energy absorbed prior to maximum load ($U_{\sigma max}$), which is the integral of the

stress-strain curve until $\varepsilon_{\sigma max}$. In the subsequent analysis, the influence of the radiation dose received by the material on these mechanical properties has been evaluated.

3.4.- Fractography

After performing the tensile tests, the fracture surface of the specimens was examined by Scanning Electron Microscopy (SEM) using a Carl Zeiss™ device, model EVO MA15, equipped with detectors for secondary and retrodispersed electrons as well as X-rays (Oxford Instruments^{TM}). The aim of these observations is to identify the mechanisms of failure undergone by the material as well as the possible influence of the irradiation.

3.5.- Raman spectroscopy

In this study, Raman spectroscopy[14][15][16] was employed to identify the microstructural changes induced by the different sources of radiation (X rays, gamma rays or neutrons) at the molecular level. The Raman spectra were taken at room temperature under atmospheric pressure in backscattering geometry with a Horiba T64000 triple spectrometer using the 514.5 and 647.0 nm lines of a Coherent Innova Spectrum 70C Ar+-Kr+ laser, and a nitrogen-cooled CCD (Jobin-Yvon Symphony) with a confocal microscope and a 100X objective for detection. The integration time was 20 s and the power was kept on the sample below 5 mW to avoid laser-heating effects on the probed material and the concomitant softening of the observed Raman peaks. With these experimental conditions, laser wavelength λ = 647.0 nm and a microscope objective of 100X with a numerical aperture of NA = 0.85, a focal spot of 0.93 μm (1.22λ/NA) and a resolution depth of about 0.9 μm (λ/NA2) were obtained.

3.6.- Statistics

Several statistical techniques were used in this research. The means of distributions were compared using t-tests or the ANOVA (analysis of variance) test. Previously, the normality of the data distributions was verified through the Kolmogorov–Smirnov test (this test returns a test decision for the null hypothesis that the data comes from a standard normal distribution, against the alternative hypothesis that it does not follow such a distribution). For multiple comparisons between variables, the Tukey test was applied. In all cases, a p-value of less than 0.05 was considered significant. Several populations of data were represented using box-and-whiskers plots; the data points that lied outside of the fence values were considered as outliers; the mean of the distribution was represented as a black square.

4. EXPERIMENTAL RESULTS

4.1. Chemical characterization

The chemistry of randomly selected samples was determined by means of (FT-IR) spectroscopy. The device automatically identifies the constituent material of the sample by locating the experimental spectrum in a database. In this case, the material was identified as polyurethane; the comparison between the experimental and the reference spectra is shown in Fig. 4. According to the TGA, which is represented in Fig. 5, the polymer amounts to 86.9%, the black carbon to 10.0% and the remainder (3.1%) corresponds to the inorganic residue present.

Figure 4. Comparison between the FT-IR spectra of sample and that of the polyurethane (database).

Figure 5. Result of the TGA analysis.

4.2.- Tensile tests

An example of a specimen stretched during a tensile test can be seen in Fig. 6, which allows the extraordinary ductility of this material to be appreciated. In order to minimize the number of failed tests due to the fracture of the specimen at its ends (which would be a symptom of the local damage created by the clamping system, falsifying the actual strength of the material), the ends of the specimens were protected with two rubber sheets. Even although this method provides a good grip, some tests were discarded because of the relative sliding between the specimen and the clamps. The stress-strain curves of the valid tests of the six groups comprised in this study are represented in Fig. 7; to facilitate the comparison, the same scales were used for the graphs. Table 2, in turn, gathers some relevant statistics (mean, standard deviation and coefficient of variation) for the three mechanical parameters analyzed (σ_{max}, $\varepsilon_{\sigma max}$ and $U_{\sigma max}$). Note that, in general, the experimental curves belonging to the same group have substantial dispersion. For this reason, in order to establish comparisons between groups or determine trends, statistical techniques have been used, as explained in Section 5.

Figure 6. Polyurethane specimen being stretched during a tensile test.

Figure 7. Stress-strain curves obtained for each of the groups involved in the study: (a) control group, (b) 20.5 kGy, (c) 100 kGy, (d) 300 kGy, (e) 900 kGy, (f) neutrons ($7.23 \cdot 10^{10}$ n/cm^2).

Table 2. Statistical summary (including the mean, standard deviation and coefficient of variation) of the three mechanical parameters analyzed in the study (σ_{max}, $\varepsilon_{\sigma max}$ and $U_{\sigma max}$).

		σ_{max} (MPa)	$\varepsilon_{\sigma max}$ (mm/mm)	$U_{\sigma max}$ (10^{-3} J/mm^3)
Control	Mean	33.08	15.65	271.78
	Standard deviation	7.23	1.59	48.19

	Coefficient of variation (%)	21.86	10.18	17.73
X-rays (20 kGy)	Mean	23.70	13.69	210.10
	Standard deviation	6.83	5.23	104.12
	Coefficient of variation (%)	28.81	38.23	49.56
X-rays (100 kGy)	Mean	28.16	14.09	235.53
	Standard deviation	8.93	3.91	112.56
	Coefficient of variation (%)	31.69	27.76	47.79
X-rays (300 kGy)	Mean	23.44	12.29	172.82
	Standard deviation	4.47	1.90	53.77
	Coefficient of variation (%)	19.07	15.46	31.11
X-rays (900 kGy)	Mean	17.83	6.99	76.77
	Standard deviation	1.31	0.80	12.96
	Coefficient of variation (%)	7.38	11.42	16.89
Neutrons ($7.23 \cdot 10^{10}$ n/cm^2)	Mean	37.46	17.05	341.13
	Standard deviation	3.77	0.50	24.07
	Coefficient of variation (%)	10.1	2.9	7.1

4.3.- Fractography

In this section, the results of the fractographic study carried out by SEM are shown aiming at correlating the previously described behavior patterns with the failure mechanisms undergone by the material. Thus, in Fig.8, three fractographs are collected, being representative of the typical appearance of the fracture surface of a sample of the control group (Fig.7(a)), a sample irradiated up to 900 kGy and a sample irradiated with neutrons, respectively. Some micrographs with greater magnification have been selected to allow the details to be appreciated.

Figure 8. SEM micrographs showing the fracture surface of selected samples after the tensile test. (a) Control group, (b) 900 kGy, (c) neutrons ($7.23 \cdot 10^{10}$ n/cm^2).

In Fig. 8(a) (non-irradiated material) the fracture surface shows evident signs of ductile tearing. Surface irregularities, cavities and discontinuities are observed, revealing the

high plastic deformation undergone by the material before the final fracture. It is worth noting that the fracture mechanisms observed in Fig. 8(a) are common, with minor random differences, to the rest of samples irradiated up to 300 kGy. None of these features is present in the fractography depicted in Fig. 8(b) (polyurethane exposed to 900 kGy). In this case, the fracture surface is essentially flat, typical of a material that has undergone brittle fracture, with restricted ability to store plastic deformation energy during the failure. These features are evident signs of irradiation embrittlement. In the left part of the picture, the region in which the fracture has originated is observed, as well as the lines of crack growth starting from it. Only the right side of the fractography shows a limited amount of surface irregularity, corresponding to the plastic deformation of the material in the final remaining ligament. The similarities between the features present in Fig. 8(a) (control group) and Fig. 8(c) (samples exposed to neutron irradiation) are evident. The mechanisms of fracture experienced by the material are very similar, proving also in this case the existence of a highly ductile failure process.

4.4.- Raman spectroscopy

Polyurethane shows higher radiation resistance than other common polymers, such as polyolefins and vinyl polymers [17]. However, the effects of irradiation on the microstructure are complex and closely related to the chemical composition, irradiation environment, and absorbed dose [18]. Fig. 9 shows the Raman spectra of the samples exposed to 0, 20.5, 100, 300 and 900 kGy, respectively. The Raman wavenumber (or, equivalently, frequency) for the non-irradiated sample (1304.5 cm^{-1}) is represented as a vertical dotted line, making it possible to appreciate the displacement of this peak as a function of the dose.

Figure 9. Experimental Raman spectrum (black continuous line) and fitting (red solid line) of a sample of polyurethane exposed to a dose of 900 kGy.

The band for a non-irradiated sample at a wavenumber of 1304.5 cm^{-1} has been used as a reference to characterize the molecular condition of polyurethane as a function of the radiation exposure. This band is associated with the vibration of the C-H bending bonds present in the polyurethanes and is related to the structural stability of the material [19], [20]. For this reason, the wavenumber of this band has been measured as a function of the dose; the results are represented in Fig. 10 (note that the angular frequency, $\omega=\nu/2\pi$, is represented, rather than the frequency, ν). As can be seen, the frequency of this mode decreases with increasing doses of electromagnetic radiation, which is indicative of the existence of a process of destabilization of the material at the molecular level. The points were fitted to a straight line, as shown in the figure.

Figure 10. Influence of the exposure dose (kGy) on the vibration frequency of the C-H bending bonds (ω_{CH}) obtained through Raman spectroscopy.

Fig. 11 compares the spectrum of one of the non-irradiated samples against that of a sample exposed to neutron irradiation. As can be seen, the dose of neutron irradiation does not alter the frequency of the CH bending band; moreover, the Raman peaks are thinner, indicating that this type of radiation has little effect on the crosslinking of the samples based on soft segments[21][22].

Figure 11. Comparison of the Raman spectrum of a non-irradiated sample (0 dose) and a sample exposed to neutron irradiation.

5. DISCUSSION

This research was aimed at determining the influence of electromagnetic (X or gamma rays) or neutron irradiation on the mechanical response (strength, ductility and toughness) of the polyurethane part of a series of polyurethane joints. In order to establish trends, the means of the three mechanical parameters selected (σ_{max}, $\varepsilon_{\sigma max}$ and $U_{\sigma max}$) were plotted in the panel in Fig. 12 as a function of the dose they were exposed to. In addition, Fig. 13 shows an equivalent representation for the neutron irradiation. Regarding X and gamma rays, the data plotted in Fig. 12, including the standard deviations were fitted with a linear model. In all cases, a negative slope was obtained, and the values of the coefficient of determination, R^2, indicated a strong correlation (particularly for the ductility, $\varepsilon_{\sigma max}$, where $R^2 \approx 0.96$). Concerning the effects resulting from exposure of polyurethane to neutron irradiation, the plots collected in Fig. 13 give the impression that the three properties studied have undergone a slight increase after exposure. This effect is particularly noticeable for the material toughness (assessed through $U_{\sigma max}$). Therefore, the first noteworthy conclusion is that, for the doses and fluences used in this study, electromagnetic radiation negatively affects the mechanical behavior of the polyurethane while the neutron irradiation produces a slight increase.

Figure 12. Correlation between the mechanical parameters σ_{max}, $\varepsilon_{\sigma max}$ and $U_{\sigma max}$ and the dose of X or gamma rays they were exposed to.

Figure 13. Influence of the neutron irradiation on the mechanical properties σ_{max}, $\varepsilon_{\sigma max}$ and $U_{\sigma max}$.

The trends followed by the mean values, represented above, provide valuable information. Nevertheless, in spite of the impressions that could be derived from Fig. 12 and Fig. 13, the scatter of the data should be taken into consideration for a rigorous

assessment of the effects derived from the exposure of the polyurethane to the X or gamma rays or to neutron irradiation. For this reason, the ANOVA and the Tukey tests were used to assess the variance of the means corresponding to different doses of X or gamma rays, while the t-test was employed in the case of the neutron irradiation. The data for each of the mechanical parameters shown in Fig. 14 as boxplots (note that the boxplot to the right in each of the plots corresponds to the group of samples exposed to neutron irradiation), making it possible to appreciate the scatter of the results. For convenience, without loss of being representative, the outliers of the distributions were removed from the plots.

Figure 14. Boxplots corresponding to the selected mechanical parameters. (a) σ_{max}, (b) $\varepsilon_{\sigma max}$, and (c) $U_{\sigma max}$. The outliers were removed from the distributions.

The visual inspection of the data represented in Fig. 14 allows a common pattern of behavior to be identified for the three mechanical properties. Thus, taking into account the scatter of results, there appears to be no net effect of the X or gamma rays for doses below 300 or 900 kGy. Moreover, neutron exposure has hardly affected any of the mechanical parameters. In order to assess this evidence more accurately, a series of statistical comparisons have been carried out. Thus, the ANOVA test was used with each of the three mechanical properties to compare the means of the distributions corresponding with different levels of X or gamma ray doses (removing the outliers). Previously, the Kolmogorov–Smirnov test was employed to validate that each of the 18 populations (three mechanical properties and six material conditions) followed a Gaussian distribution. The minimum p-value obtained in this analysis was 0.4782, which indicates weak evidence against the null hypothesis (fail to reject). According to the results of the analysis of variance, collected in Table 3, the p-value is, for the three material properties, less than the level of statistical significance (α=0.05); hence, the

null hypothesis is rejected in all cases. In other words, the means of the distributions corresponding with different levels of X or gamma ray doses are significantly different.

Table 3: Results of the ANOVA tests (means comparison).

	p-value
$\boldsymbol{\sigma_{max}}$	6.46E-05
$\boldsymbol{\varepsilon_{\sigma max}}$	6.01E-07
$\boldsymbol{u_{\sigma max}}$	1.32E-05

Table 4 summarizes the results of the Tukey test carried out for the three mechanical parameters (previously removing the outliers). The first column shows the property analyzed. The second and third columns gather the groups that are being compared. The fourth and sixth columns collect the lower and upper limits for a 95% confidence interval. The fifth column shows the difference between the estimated group means. Finally, the seventh column contains the p-value for the hypothesis test that the corresponding mean difference is equal to zero. The paired comparisons carried out revealed some cases where the differences are significant at $p < 0.05$ (this fact is indicated by means of an asterisk on the p-value); note that, in general, the group 900 kGy is involved in this case. Hence, the material exposed to a dose of 900 kGy is significantly less ductile, less resistant and less tough than the rest of the conditions.

Table 4: Summary of results of the Tukey tests performed for the three mechanical properties (σ_{max}, $\varepsilon_{\sigma max}$ and $U_{\sigma max}$) comparing different doses of X or gamma rays.

Property	**Groups compared**		**Difference between estimated means**			**p-value**
			Lower (95%)	**Median (50%)**	**Upper (95%)**	
$\boldsymbol{\sigma_{max}}$ **(MPa)**	Control	20 kGy	-2.00	7.21	16.42	1.86E-01
	Control	100 kGy	-4.57	2.74	10.05	8.18E-01
	Control	300 kGy	1.16	8.47	15.78	1.64E-02*

	Control	900 kGy	5.94	13.08	20.21	6.68E-05*
	20 kGy	100 kGy	-13.52	-4.47	4.57	6.18E-01
	20 kGy	300 kGy	-7.78	1.26	10.30	9.94E-01
	20 kGy	900 kGy	-3.04	5.87	14.77	3.39E-01
	100 kGy	300 kGy	-1.36	5.73	12.83	1.61E-01
	100 kGy	900 kGy	3.43	10.34	17.25	1.16E-03*
	300 kGy	900 kGy	-2.31	4.61	11.52	3.28E-01
$\varepsilon_{\sigma max}$ (mm/mm)	Control	20 kGy	-3.11	1.52	6.15	8.78E-01
	Control	100 kGy	-2.55	1.13	4.80	9.02E-01
	Control	300 kGy	-0.66	2.92	6.51	1.56E-01
	Control	900 kGy	4.64	8.23	11.81	1.12E-06*
	20 kGy	100 kGy	-4.94	-0.40	4.15	9.99E-01
	20 kGy	300 kGy	-3.07	1.40	5.87	8.96E-01
	20 kGy	900 kGy	2.23	6.71	11.18	1.10E-03*
	100 kGy	300 kGy	-1.68	1.79	5.27	5.79E-01
	100 kGy	900 kGy	3.63	7.10	10.58	9.88E-06*
	300 kGy	900 kGy	1.93	5.31	8.69	6.07E-04*
$U_{\sigma max}$ (10^{-3} J/mm^3)	Control	20 kGy	-78.42	48.22	174.85	8.10E-01
	Control	100 kGy	-92.17	5.92	104.01	9.97E-01
	Control	300 kGy	-12.59	85.50	183.59	1.13E-01
	Control	900 kGy	83.45	181.54	279.63	5.15E-05*
	20 kGy	100 kGy	-164.63	-42.29	80.05	8.58E-01
	20 kGy	300 kGy	-85.06	37.28	159.62	9.05E-01
	20 kGy	900 kGy	10.99	133.33	255.67	2.68E-02*
	100 kGy	300 kGy	-12.90	79.58	172.05	1.21E-01
	100 kGy	900 kGy	83.14	175.62	268.10	3.36E-05*
	300 kGy	900 kGy	3.57	96.05	188.53	3.85E-02*

Finally, t-tests were carried out comparing the values of the control group and the results of the group of specimens subjected to neutron irradiation. As suggested above, apparently the strength, ductility and toughness of the polyurethane improves after being exposed to neutron irradiation. For this reason, two t-tests were carried out. First, a two-tailed test where the alternative hypothesis, H_a, states that the means are not equal; the p-values are gathered in the second column of Table 5 and, as can be seen, there are significant differences at the 0.05 level for both $\varepsilon_{\sigma max}$ and $U_{\sigma max}$. Next, a left-tail test was applied, where H_a establishes that the mean of the control group is less than the mean of the neutron-irradiated population. In this case (see the last column of Table

5) the differences are significant for the three material parameters. This result agrees well with the impression derived from the inspection of Fig. 13. Nevertheless, this conclusion must be taken with caution since the sample of the group of material subjected to neutron irradiation includes only three observations.

Table 5. P-values obtained in the t-tests carried out to compare the mechanical properties of the control group and the samples subjected to neutron irradiation.

	p-value (two-tailed)	**p-value (left tail)**
$\boldsymbol{\sigma_{max}}$	0.0708	0.0354
$\boldsymbol{\varepsilon_{\sigma max}}$	0.0040	0.0020
$\boldsymbol{U_{\sigma max}}$	0.0072	0.0036

The analysis of the effect derived from the exposure of polyurethane to X or gamma rays, suggests the existence of a dose threshold that must be overcome to influence the behavior of the material. For the strength of the polyurethane (measured through σ_{max}), this threshold is between 300 and 900 kGy whereas the ductility and the toughness of the material (represented by $\varepsilon_{\sigma max}$ and $U_{\sigma max}$, respectively) begins to be damaged even at a dose of 300 kGy. The influence of the X or gamma rays is detrimental for the mechanical response of the material. In contrast, the neutron irradiation of polyurethane leads to only a slight increase in σ_{max}, $\varepsilon_{\sigma max}$ and $U_{\sigma max}$.

The fractographic study has allowed the influence of irradiation on the features present in the fracture surfaces to be identified. According to these observations, a robust correlation exists between the failure micro-mechanisms developed at the fracture surface and the effect induced by the radioactive environment (X rays, gamma rays or

neutrons) on the material. From this result, the study of the fracture surface in a component of this nature that would have experienced a fracture in service (which is a very common instance in forensic engineering of failures) may be used as an indicator of the level of damage accumulated by the material under the operating conditions.

As a final contribution of this research, the microstructure of polyurethane at the molecular level has been investigated by means of Raman spectroscopy. Determining how the molecular microstructure and stability are influenced by irradiation is of great importance, not only from the basic perspective but, as we will show, from the applied viewpoint too. Raman spectroscopy is capable of identifying the chemical bands that characterize the molecular structure of polyurethanes, such as the C-H bending, as represented in Fig. 9 and Fig. 10. A strong correlation has been found between the vibration frequency of the C-H bending and the dose of exposure to electromagnetic radiation. Note in Fig. 10 that this shift is more sensitive than the mechanical material response since the frequency of the C-H bending is affected at doses of 100 kGy, well below the threshold previously identified for any of the mechanical properties. The change in crystallinity can be explained by the degree of crosslinking of the samples based on radiation crosslinking of soft segments rather than hard segments. In contrast, the vibration frequency of the C-H bending is not affected by the dose of neutron irradiation used in this research. Nevertheless, the width of the Raman peaks is reduced, which is a consequence of the fact that this type of radiation does not affect the crosslinking of the samples based on soft segments.

The correlation included in Fig. 10 opens the door for the development of Raman spectroscopy as a non-destructive tool to characterize the microstructural effect of irradiation on polyurethane. The current technological development allows the design of

a portable Raman device with an optical fiber probe to be installed in-situ, which would allow the inspection of in-service components.

6. CONCLUSIONS

The experimental work carried out in this study has made it possible to assess the modifications experienced by the elastomeric polyurethane part of a series of pneumatic clamping modules exposed to electromagnetic (X and gamma rays) or neutron irradiation. These modules operate in nuclear reactors; for this reason, they are exposed to high radioactive doses, much more demanding than those typical of most applications for this type of material. For instance, the doses of electromagnetic radiation used for sterilization rarely exceed 50 kGy; in contrast, in this research a range of doses for electromagnetic radiation up to a maximum of 900 kGy and a neutron fluence of $7.23 \cdot 10^{10}$ n/cm^2 have been employed.

The mechanical behavior of the material has been assessed from quasi-static tensile tests, to determine the tensile strength, ductility and toughness of the material. The main conclusions derived from the experimental work and the thorough statistical study carried out are summarized hereafter:

- The influence of the X or gamma rays is detrimental to the mechanical response of the material. The statistical analysis (Tukey test, significance level 0.05) has revealed the existence of a threshold dose that must be overcome to influence the behavior of the material. For the strength of the polyurethane this threshold is between 300 and 900 kGy, whereas the ductility and the toughness of the material begins to be damaged for a dose of 300 kGy.

- Neutron irradiation of polyurethane leads to a slight increase in strength, ductility and toughness. Statistics (left-tail t-test, significance level 0.05) shows that the differences are statistically significant for the three material parameters.

- A robust correlation between the mechanical properties and the fractografic features present in the samples after the tensile tests was established. For doses up to 300 kGy, fracture surfaces show evident signs of ductile tearing while samples of polyurethane exposed to 900 kGy show a fracture surface that is essentially flat, typical of an embrittled material, with a restricted ability to develop plastic deformation during the failure.

- The failure micromechanisms undergone by the material exposed to neutron irradiation are very similar to those of non-irradiated samples, corresponding to a ductile failure process.

- Raman spectroscopy has revealed a robust correlation between the vibration frequency of the C-H bending and the dose of exposure to electromagnetic radiation. The change in crystallinity can be explained by the degree of crosslinking of the samples based on radiation crosslinking of soft segments rather than hard segments. In contrast, the vibration frequency of the C-H bending is not affected by the dose of neutron irradiation (for the fluence used in this research).

This correlation between the shift undergone by the peak corresponding to the C-H bending and the radioactive exposure opens the door for the use of Raman spectroscopy as a non-destructive tool to characterize the microstructural damage induced by irradiation on polyurethane. This would be a valuable tool for the assessment of life management of polyurethane components operating in nuclear reactor environments.

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FIGURE CAPTIONS

Figure 1. (a) Sketch of a hexagonal tube-holding part consisting of three clamping modules. (b) Photograph of one of the modules.

Figure 2. Photograph allowing some of the samples available for the study to be appreciated, as well as their dimensions.

Figure 3. Description of the process developed to manufacture the tensile specimens from the polyurethane joints.

Figure 4. Comparison between the FT-IR spectra of sample and that of the polyurethane (database).

Figure 5. Result of the TGA analysis.

Figure 6. Polyurethane specimen being stretched during a tensile test.

Figure 7. Stress-strain curves obtained for each of the groups involved in the study: (a) control group, (b) 20.5 kGy, (c) 100 kGy, (d) 300 kGy, (e) 900 kGy, (f) neutrons ($7.23 \cdot 10^{10}$ n/cm^2).

Figure 8. SEM micrographs showing the fracture surface of selected samples after the tensile test. (a) Control group, (b) 900 kGy, (c) neutrons ($7.23 \cdot 10^{10}$ n/cm^2).

Figure 9. Experimental Raman spectrum (black continuous line) and fitting (red solid line) of a sample of polyurethane exposed to a dose of 900 kGy.

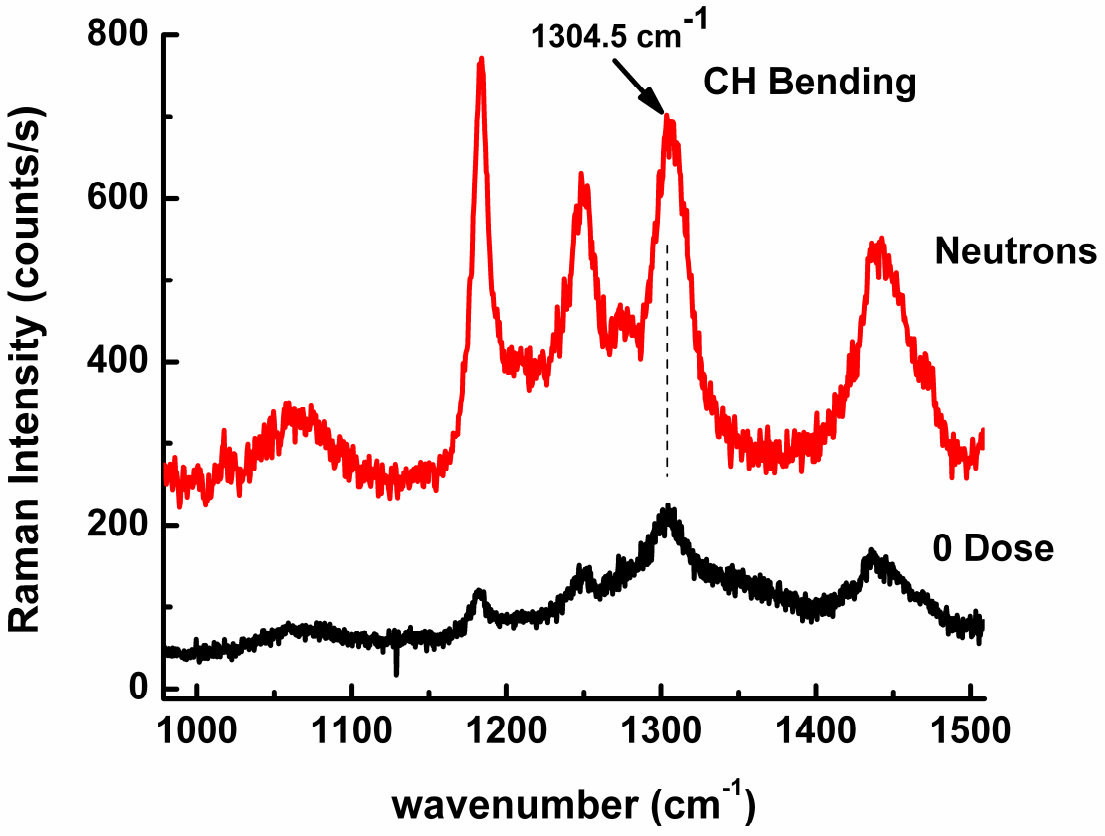
Figure 10. Influence of the exposure dose (kGy) on the vibration frequency of the C-H bending bonds (ωCH) obtained through Raman spectroscopy.

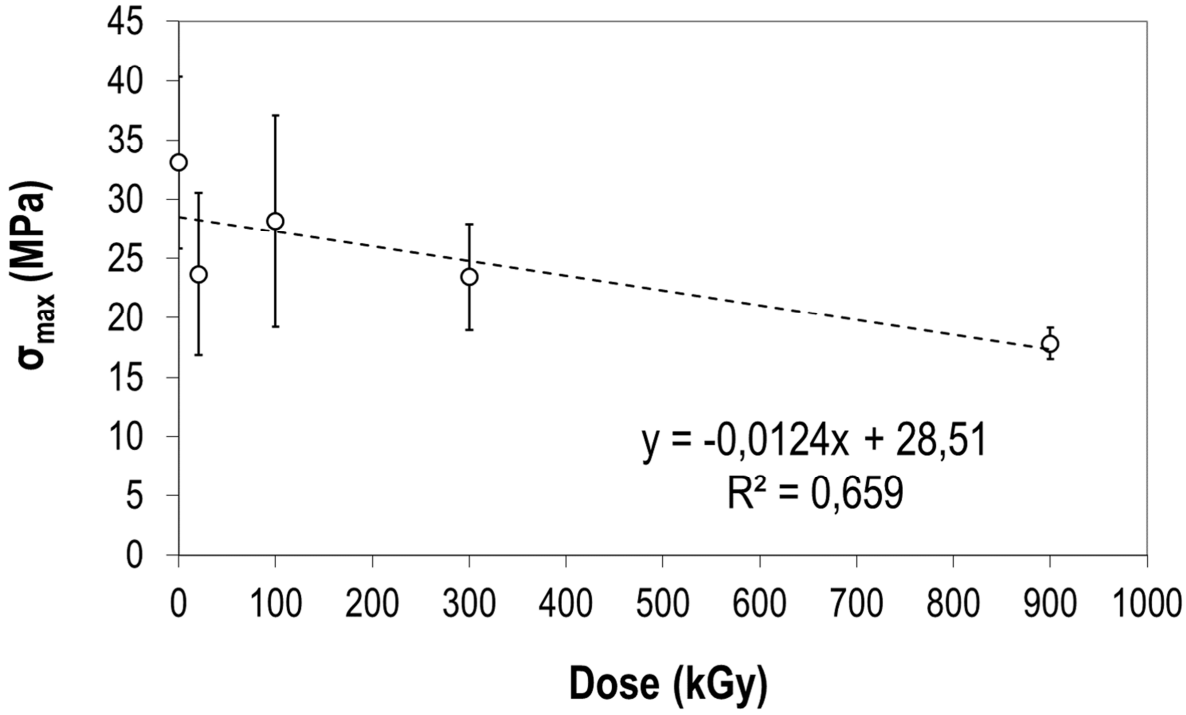
Figure 11. Comparison of the Raman spectrum of a non-irradiated sample (0 dose) and a sample exposed to neutron irradiation.

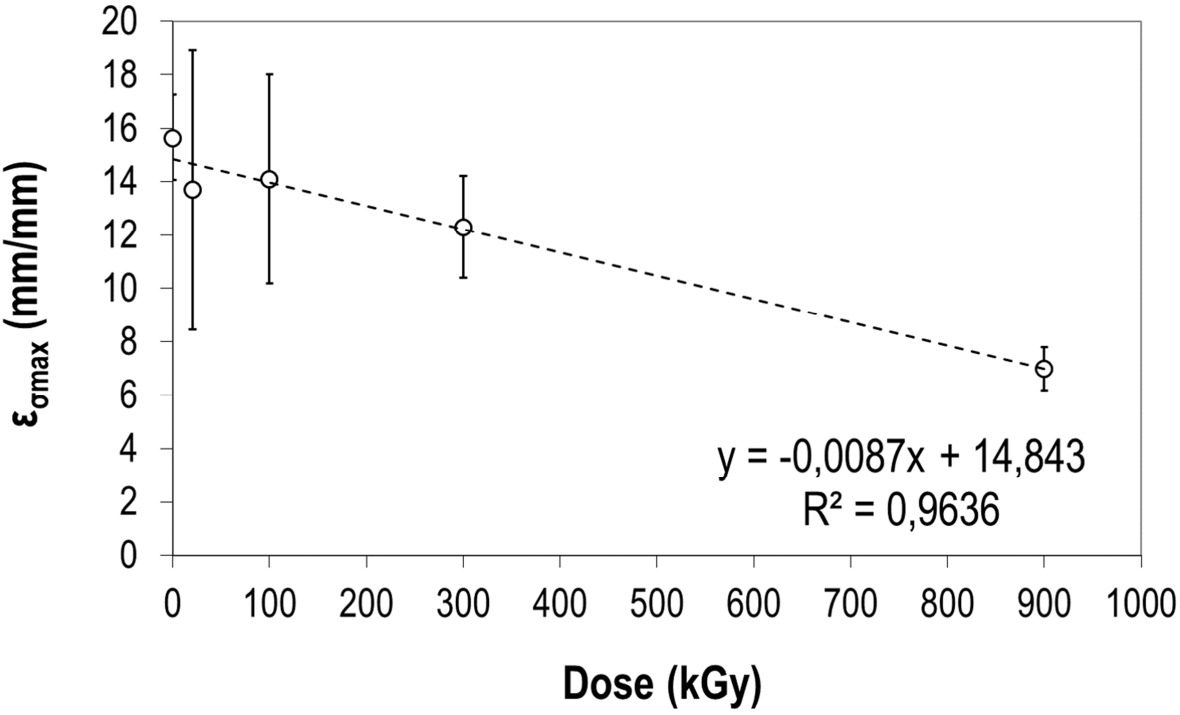
Figure 12. Correlation between the mechanical parameters σ_{max}, $\varepsilon_{\sigma max}$ and $U_{\sigma max}$ and the dose of X or gamma rays they were exposed to.

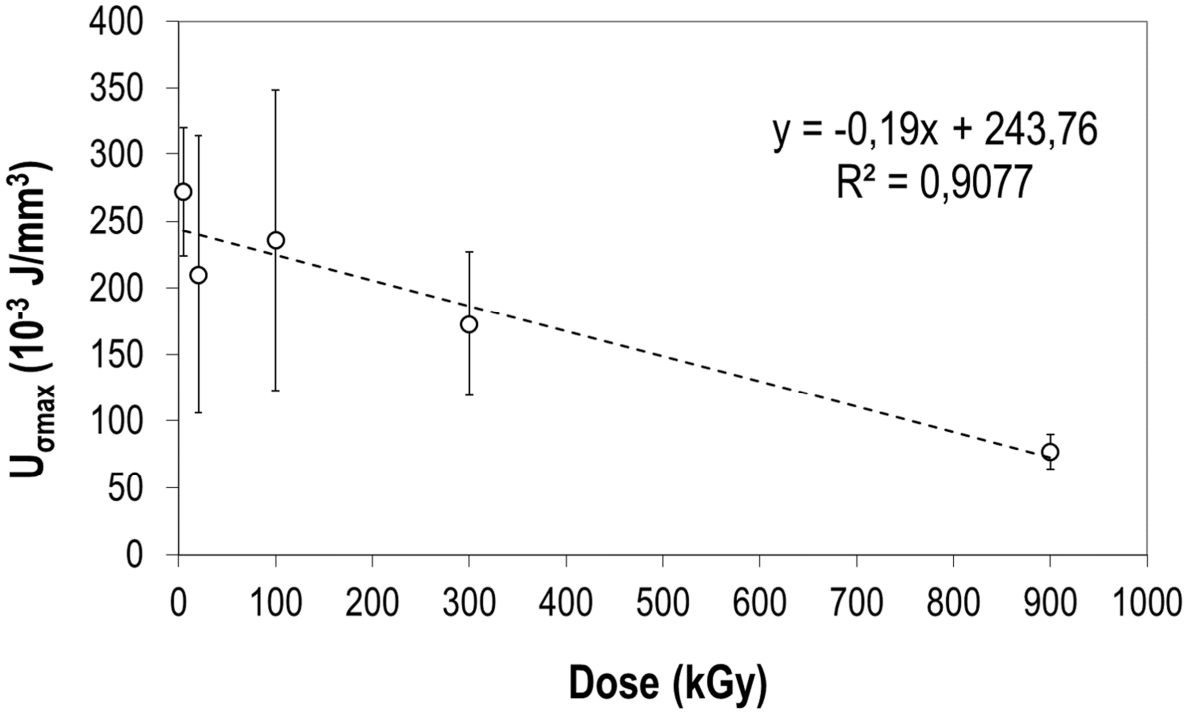
Figure 13. Influence of the neutron irradiation on the mechanical properties σ_{max}, $\varepsilon_{\sigma max}$ and $U_{\sigma max}$.

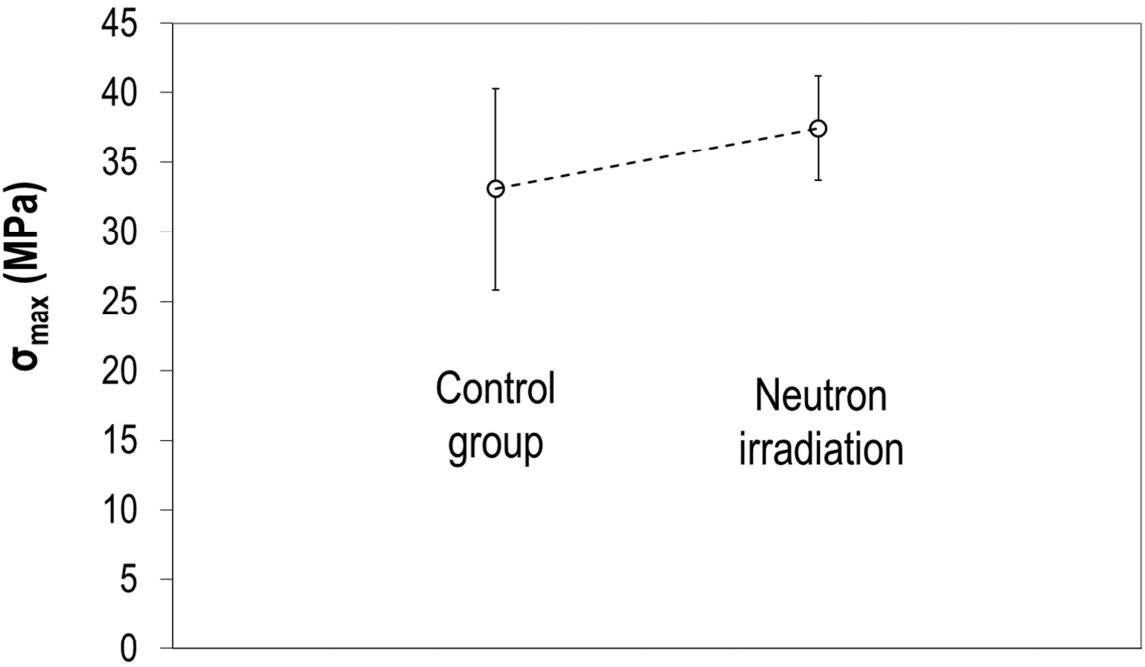
Figure 14. Boxplots corresponding to the selected mechanical parameters. (a) σ_{max}, (b) $\varepsilon_{\sigma max}$, and (c) $U_{\sigma max}$. The outliers were removed from the distributions.

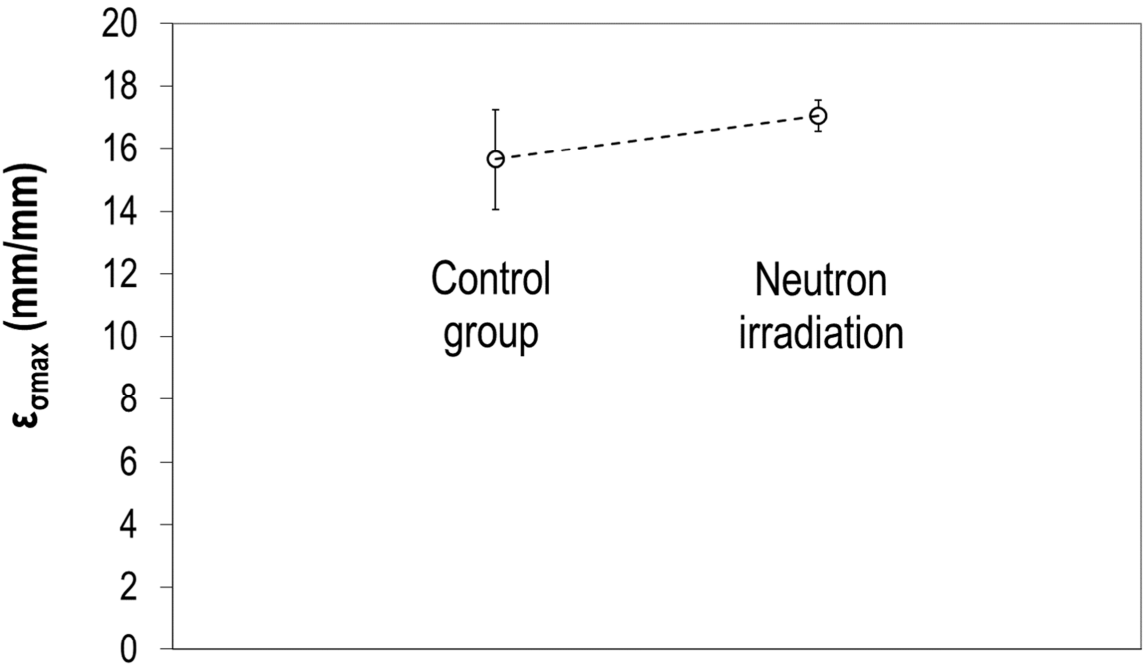


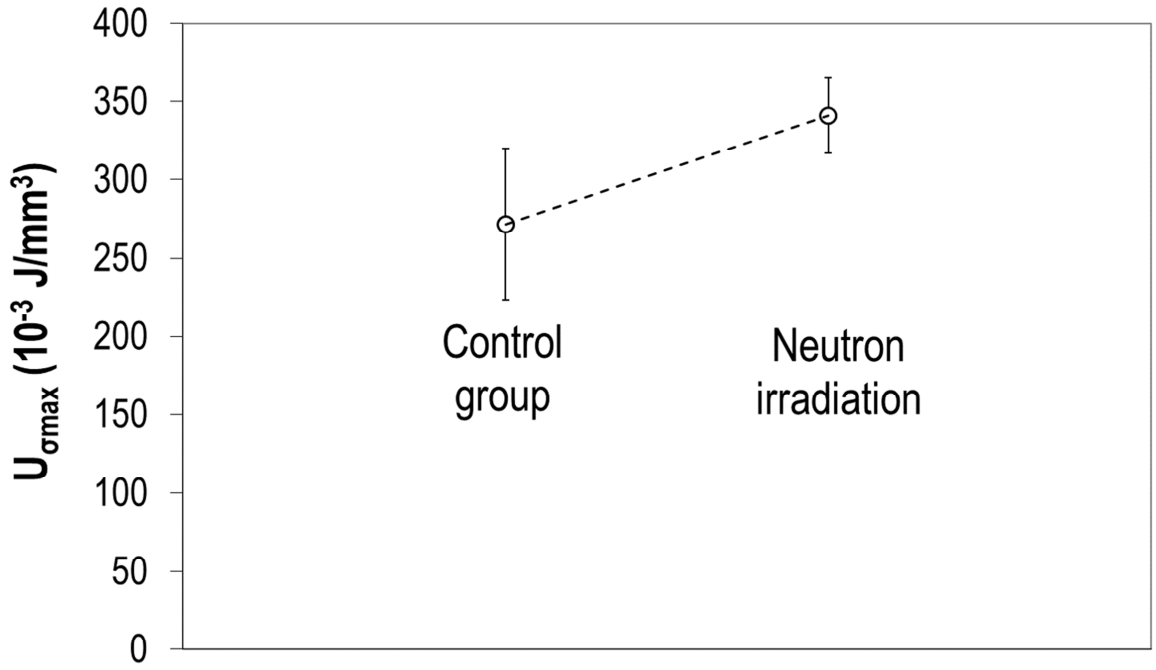


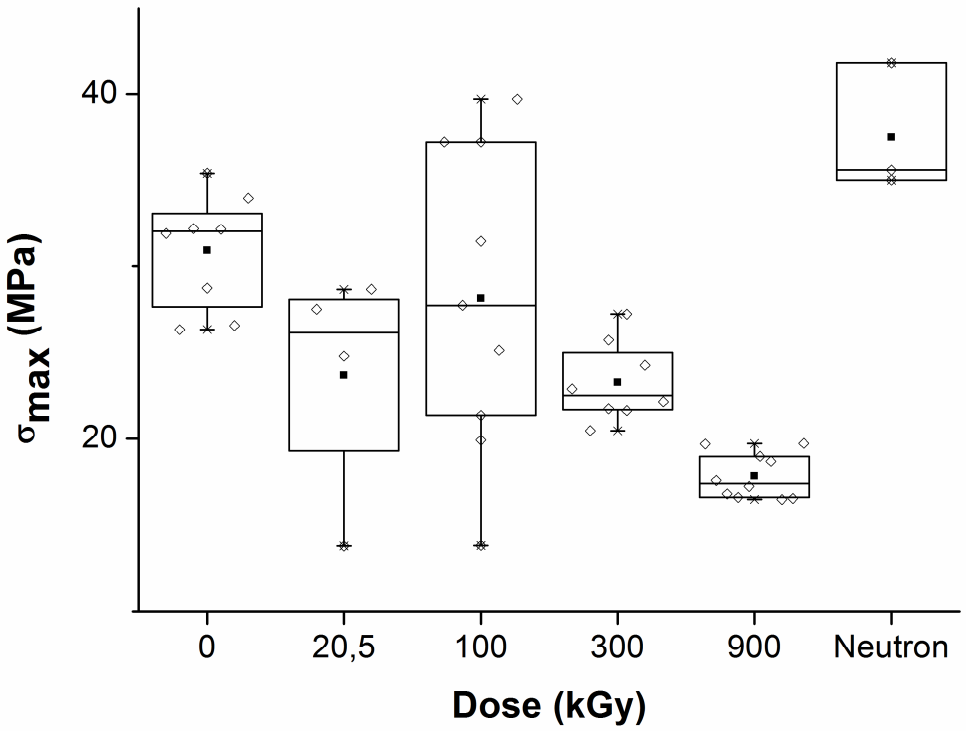


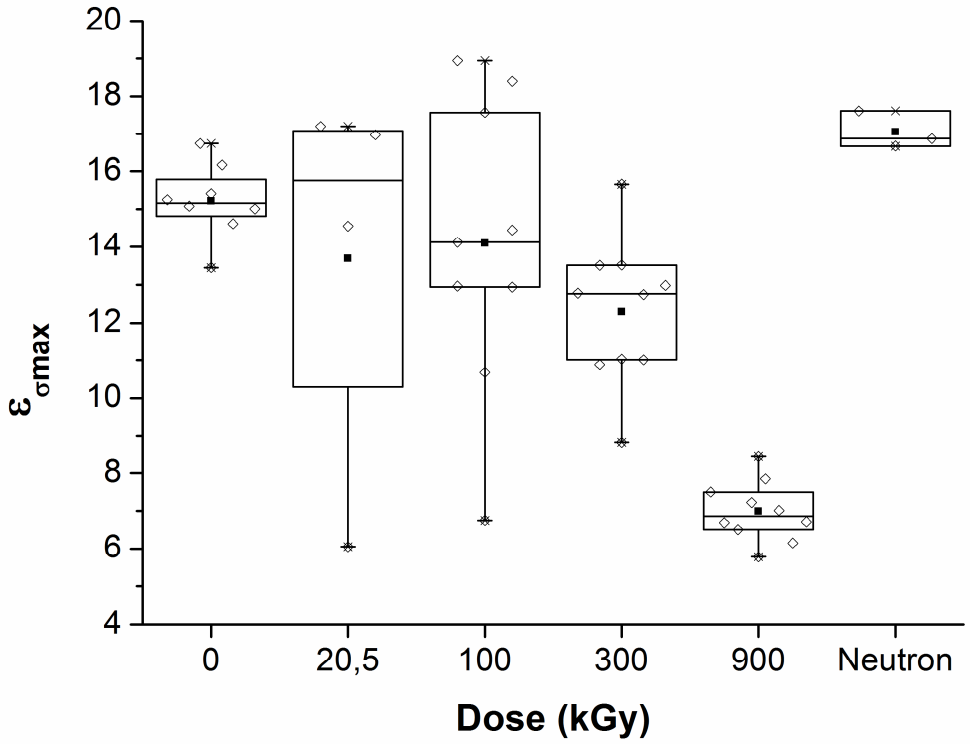


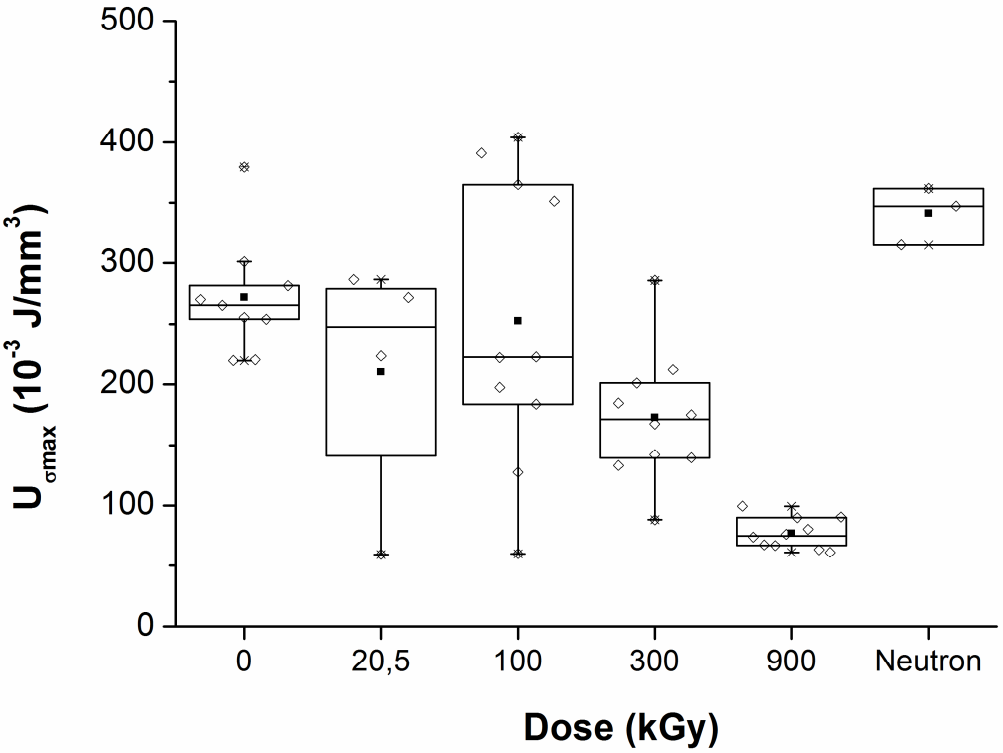


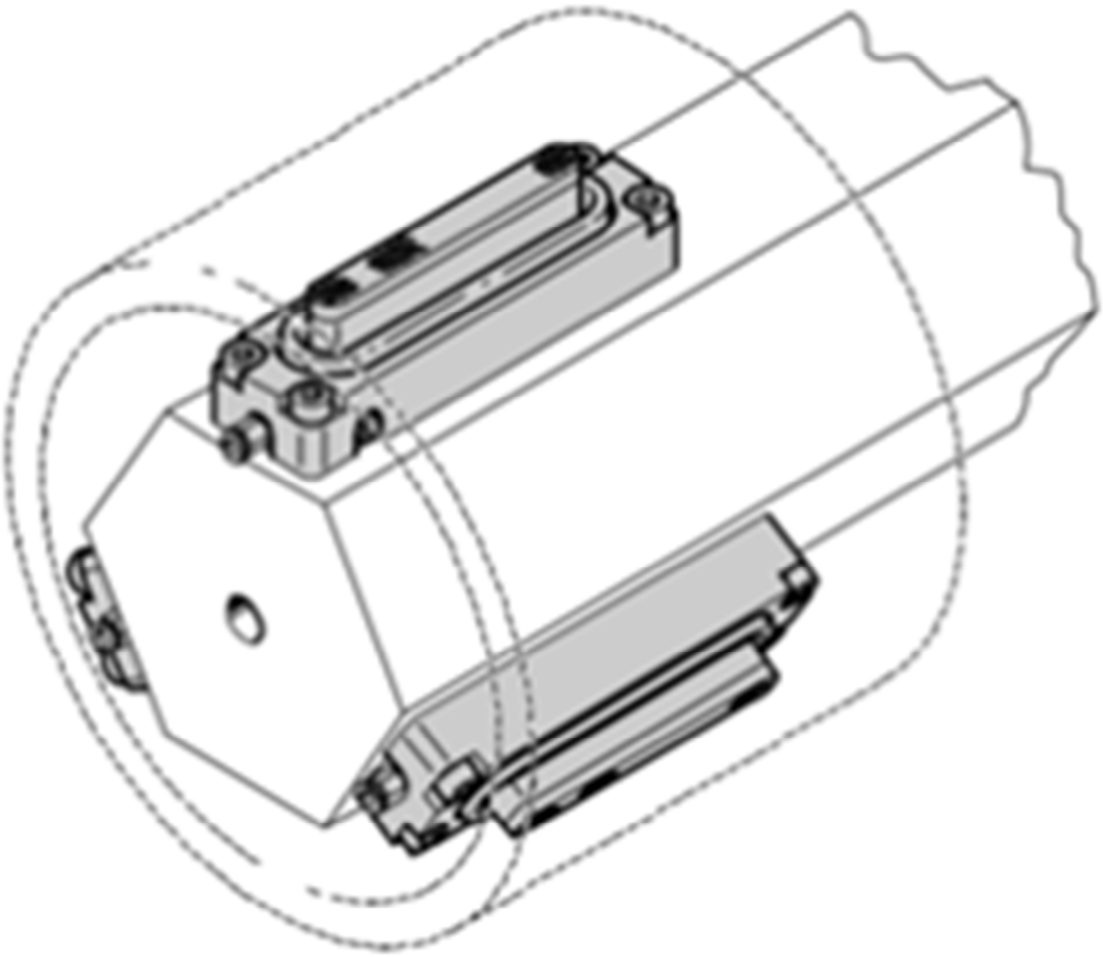


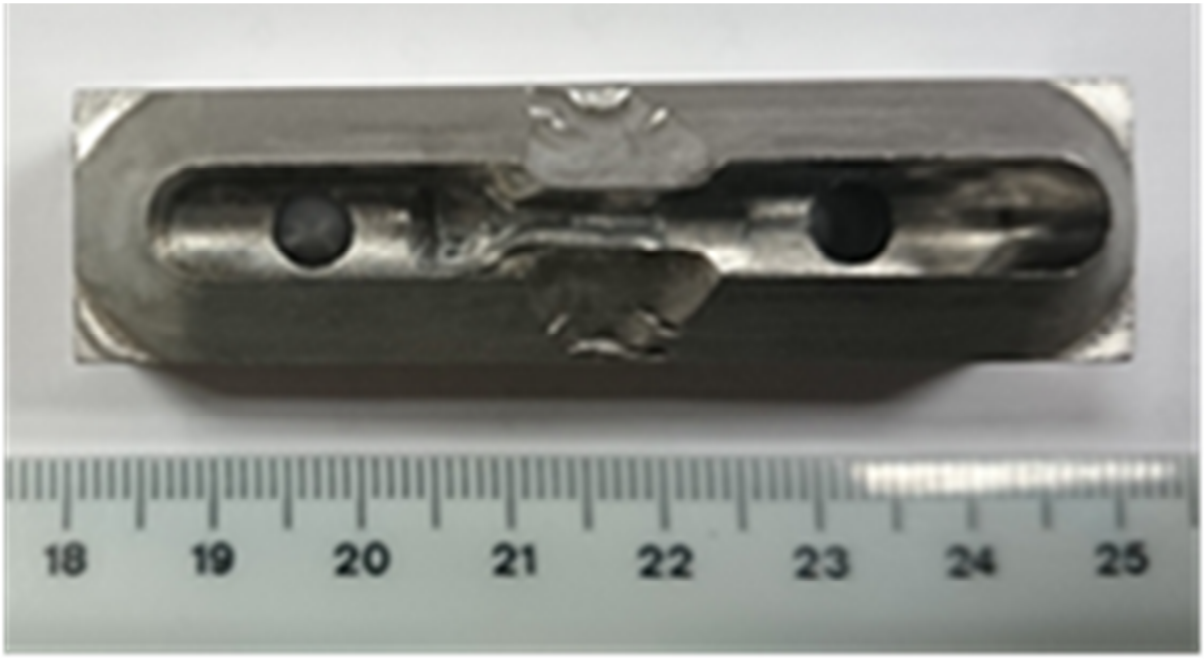


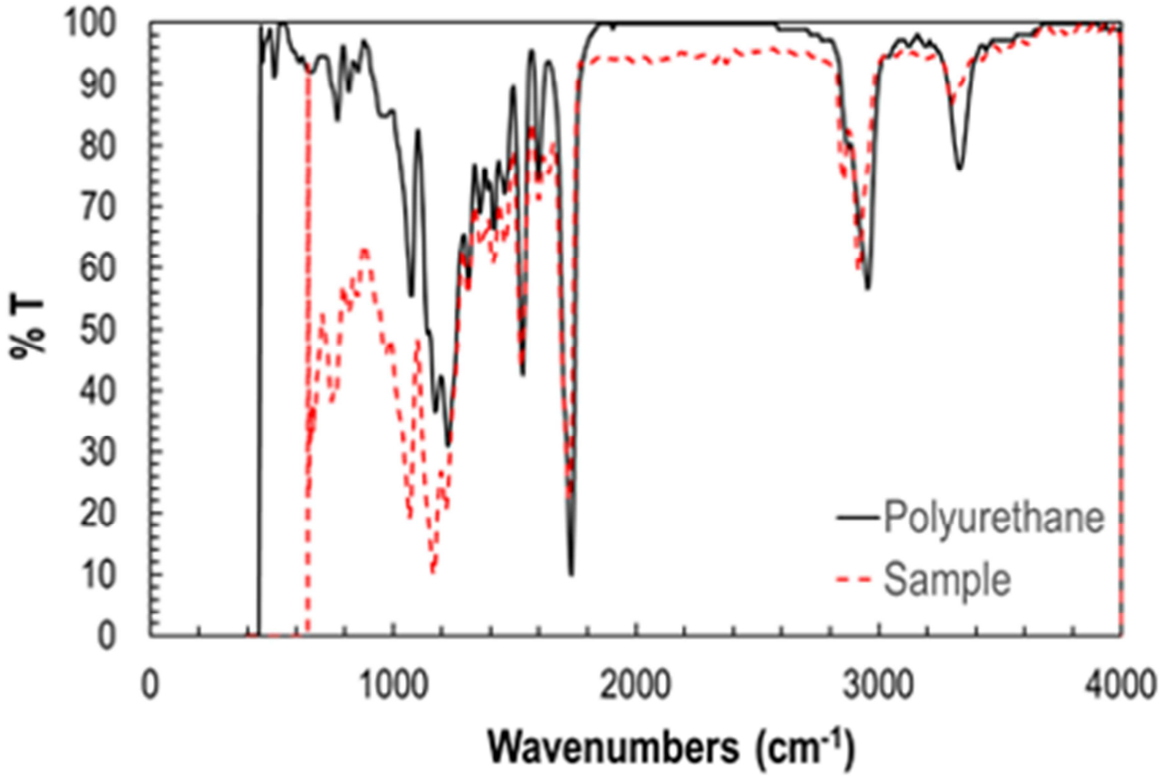


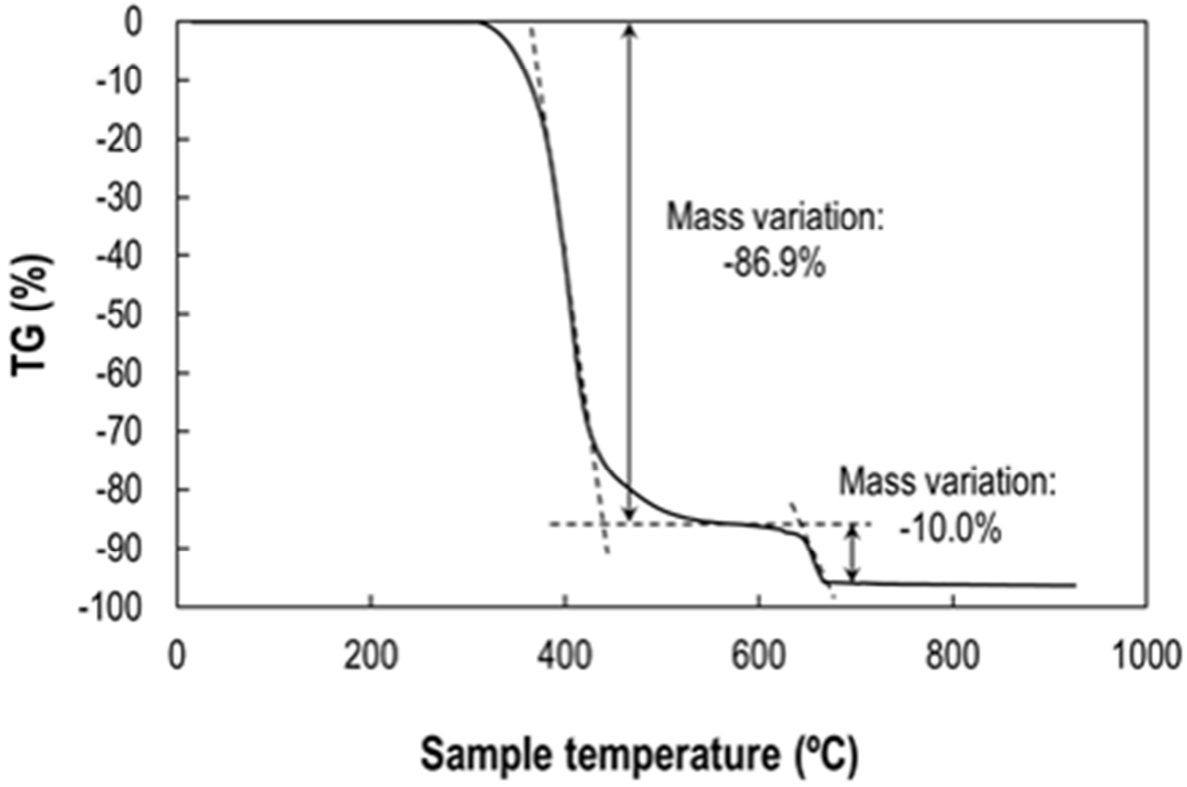


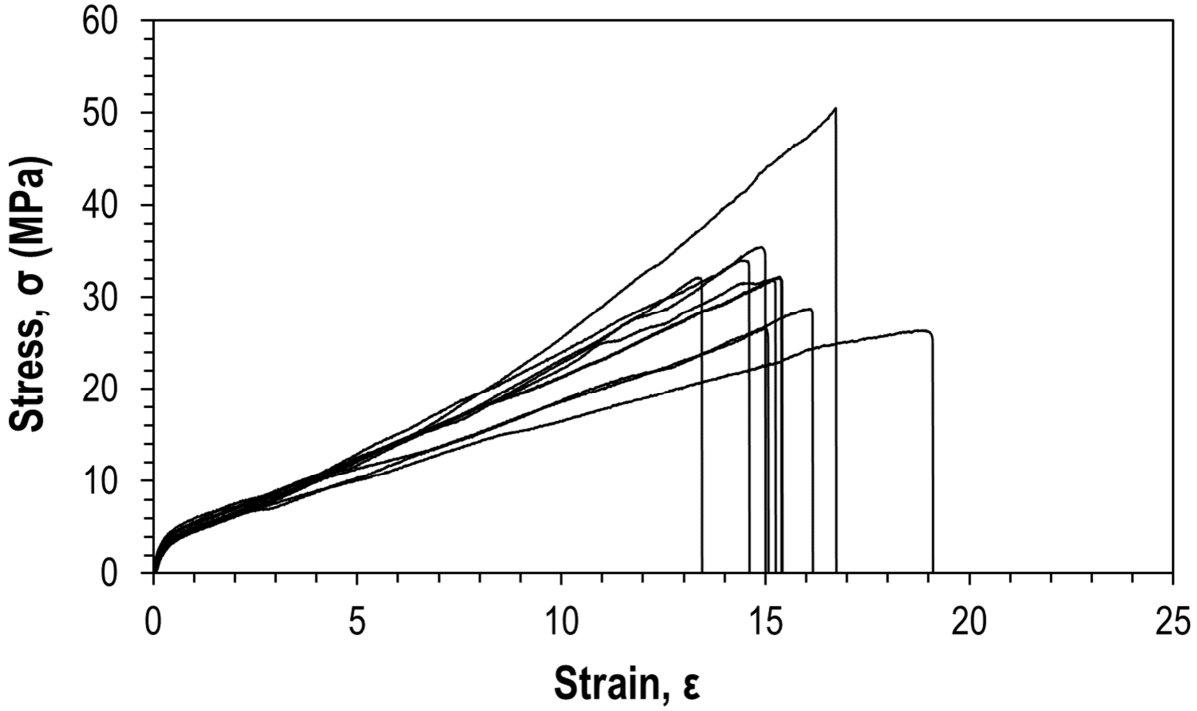


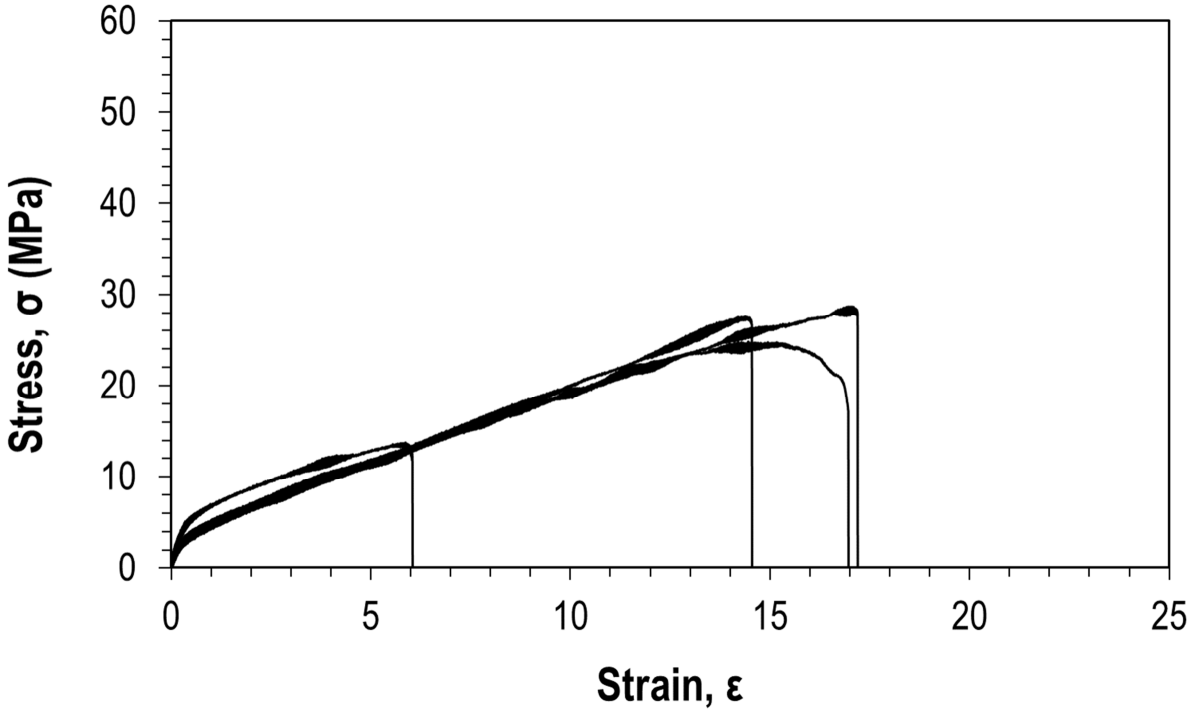


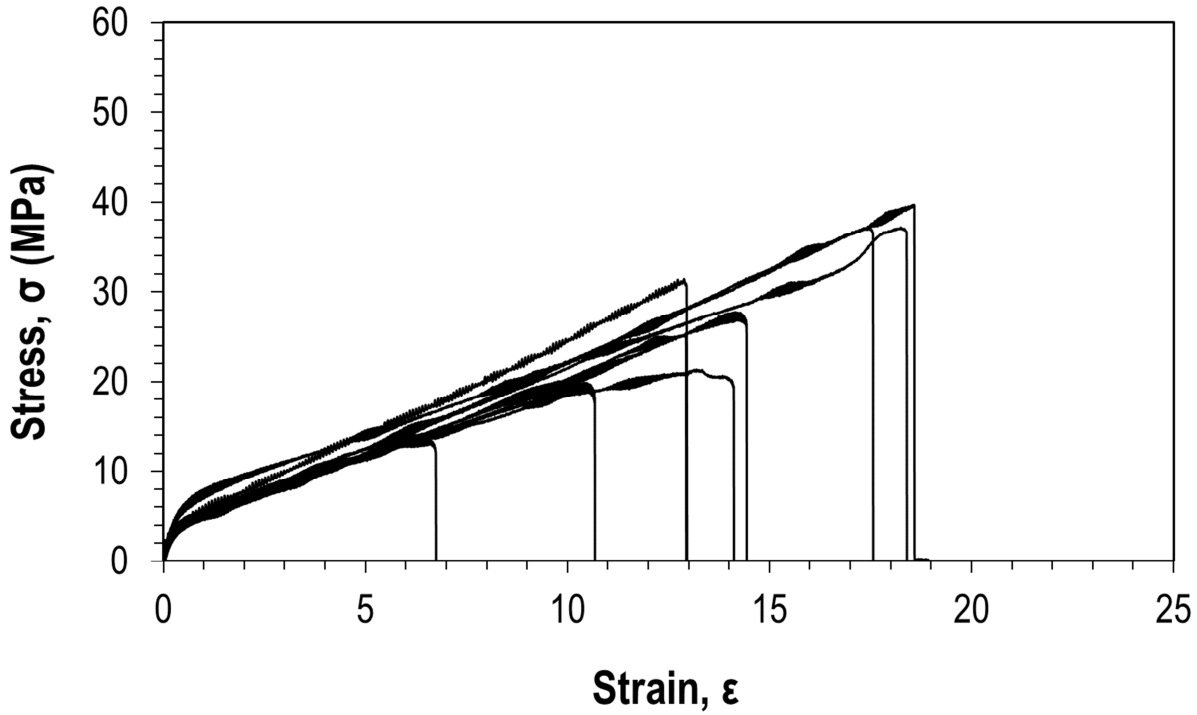


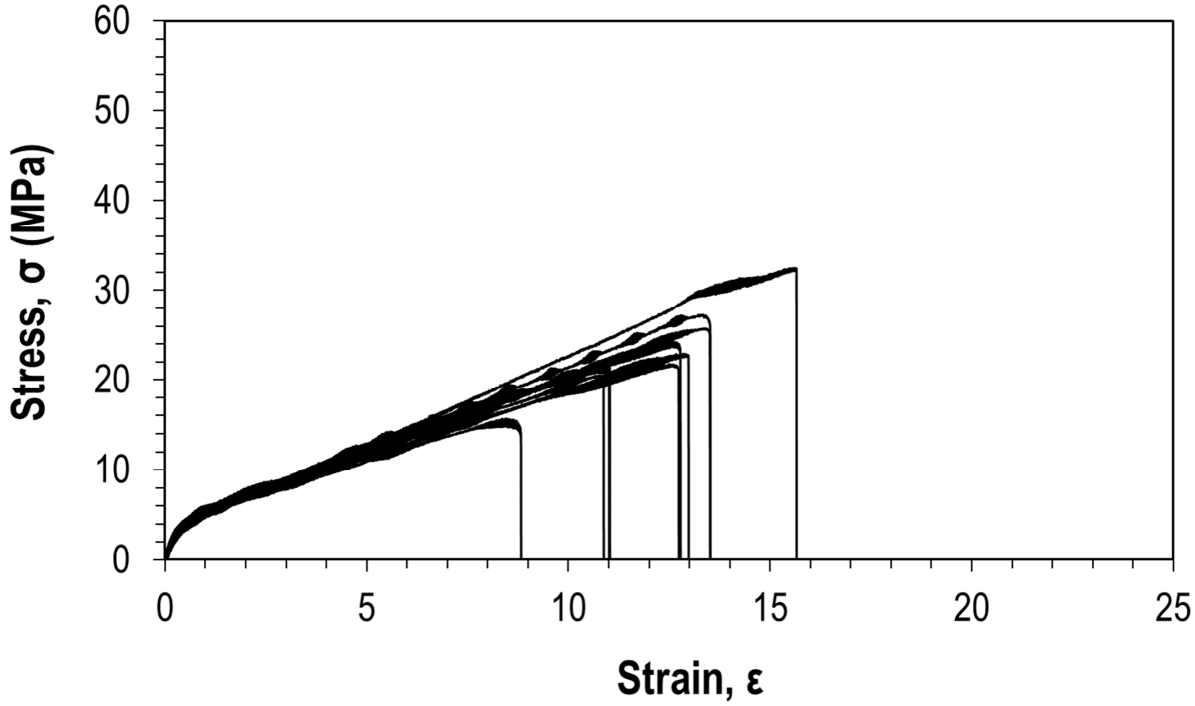


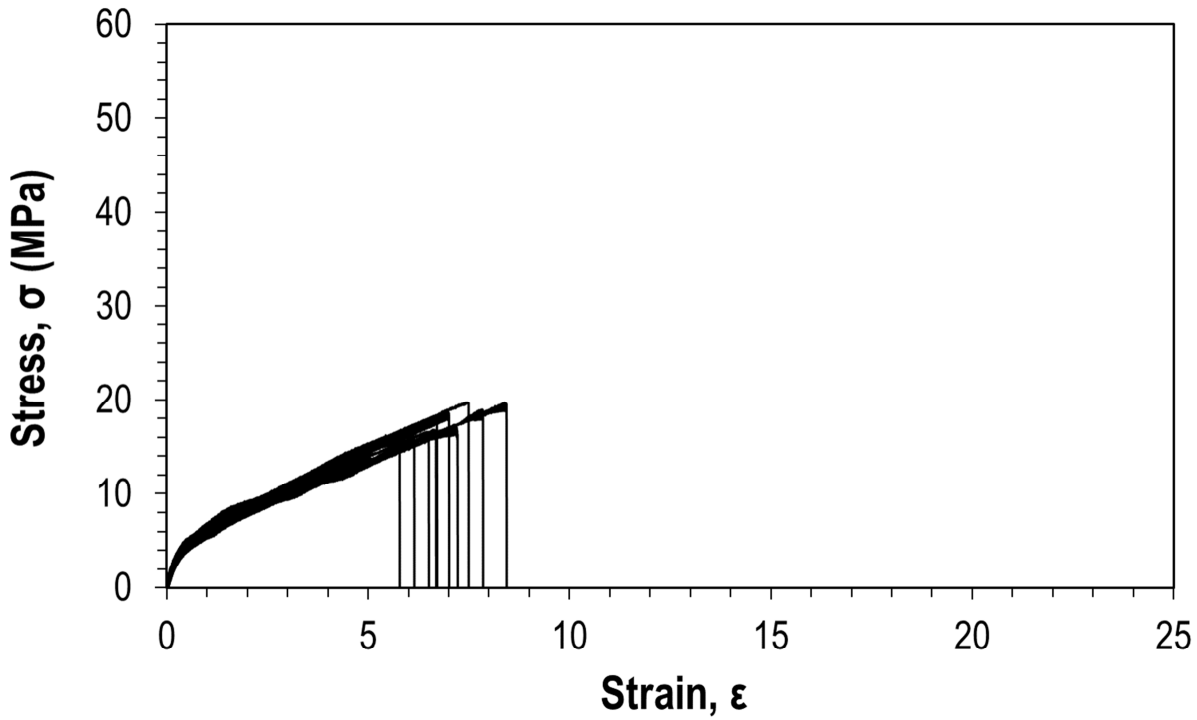


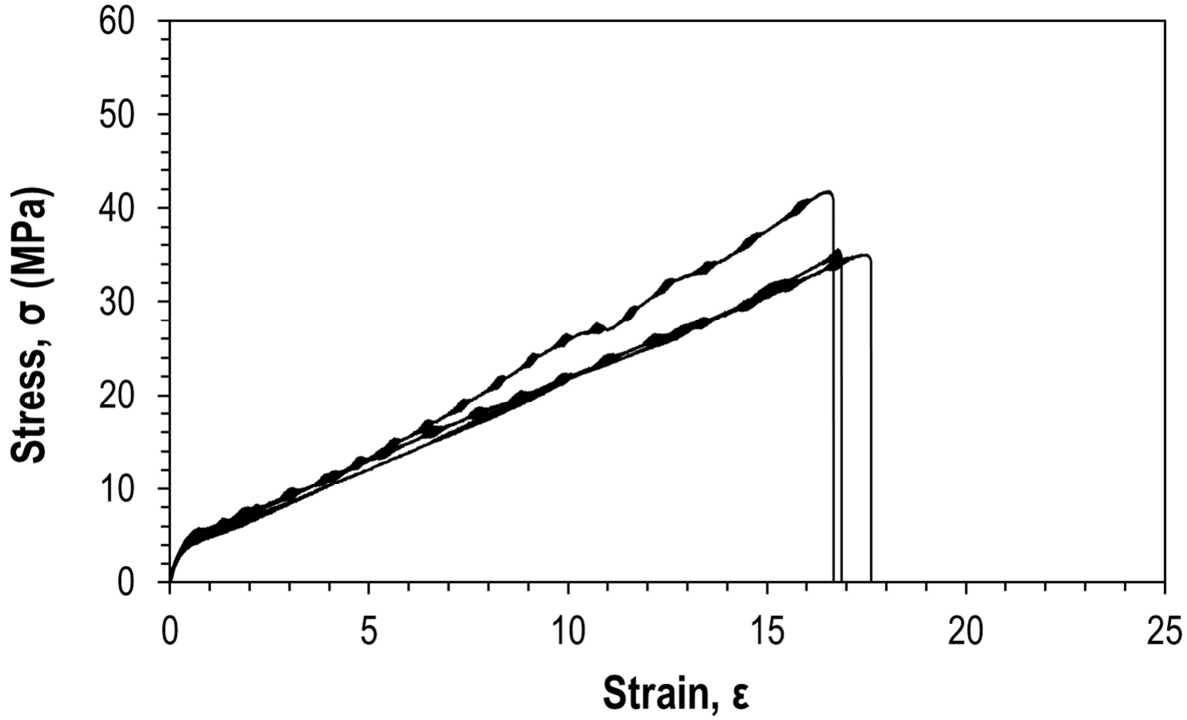


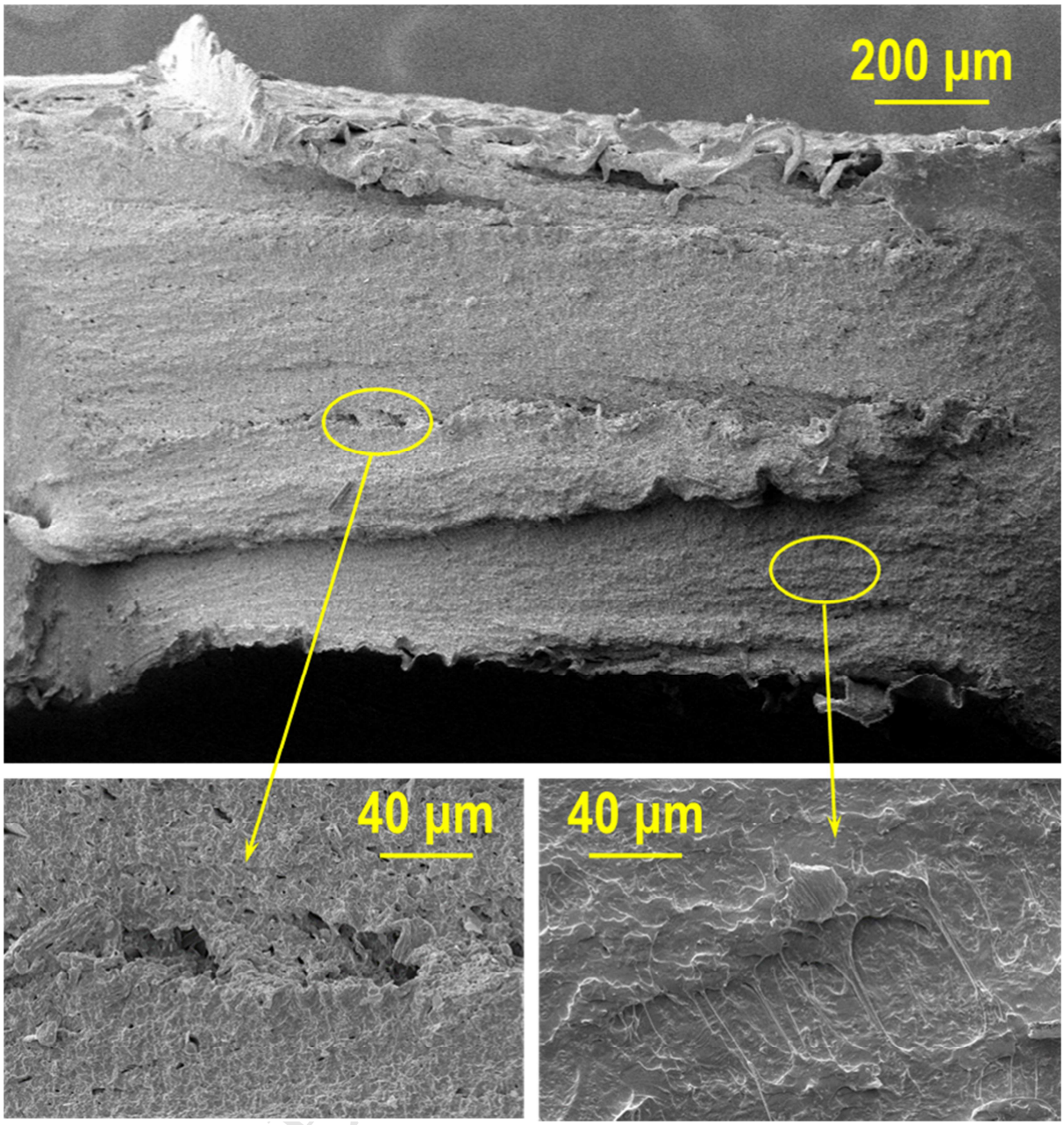


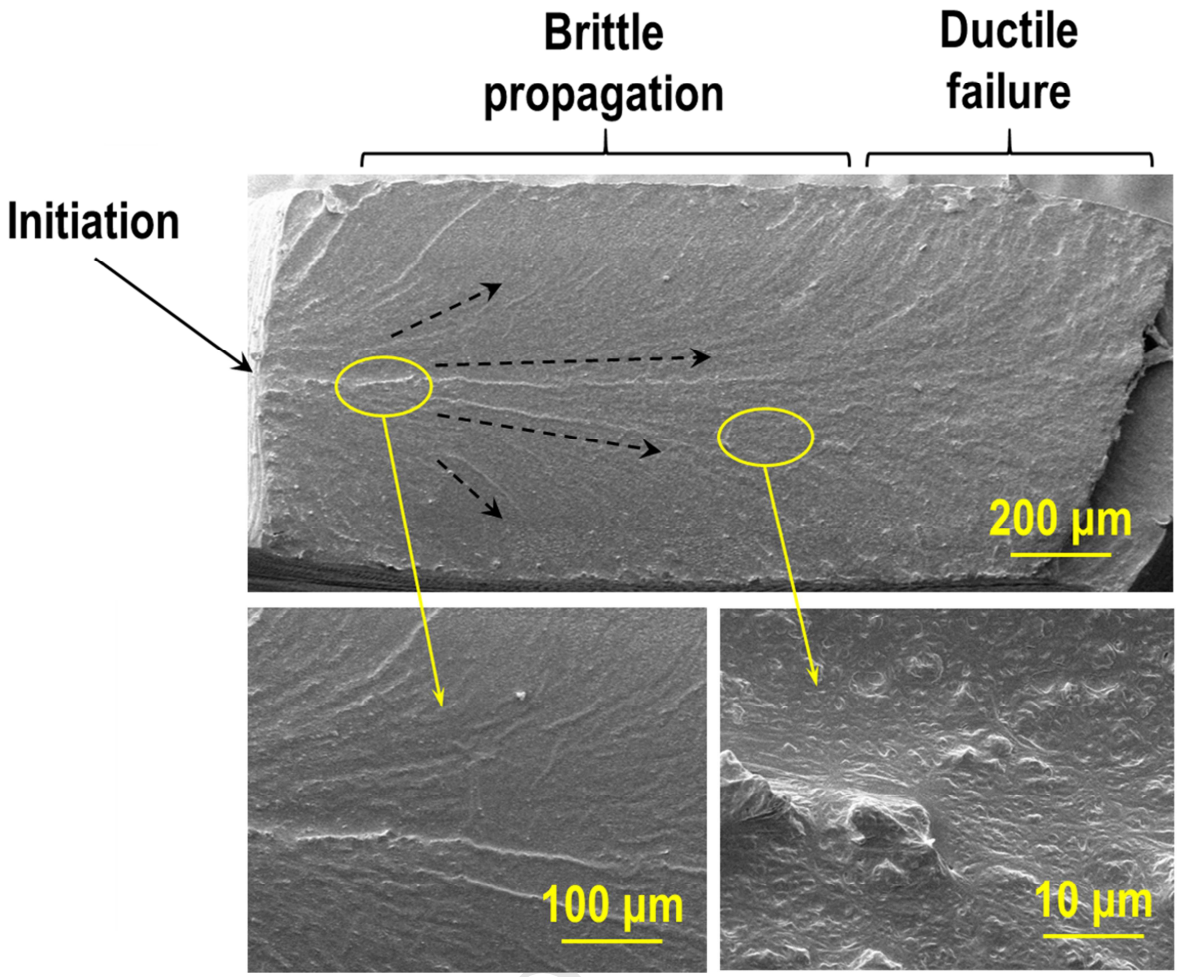











Brittle propagation
Ductile failure
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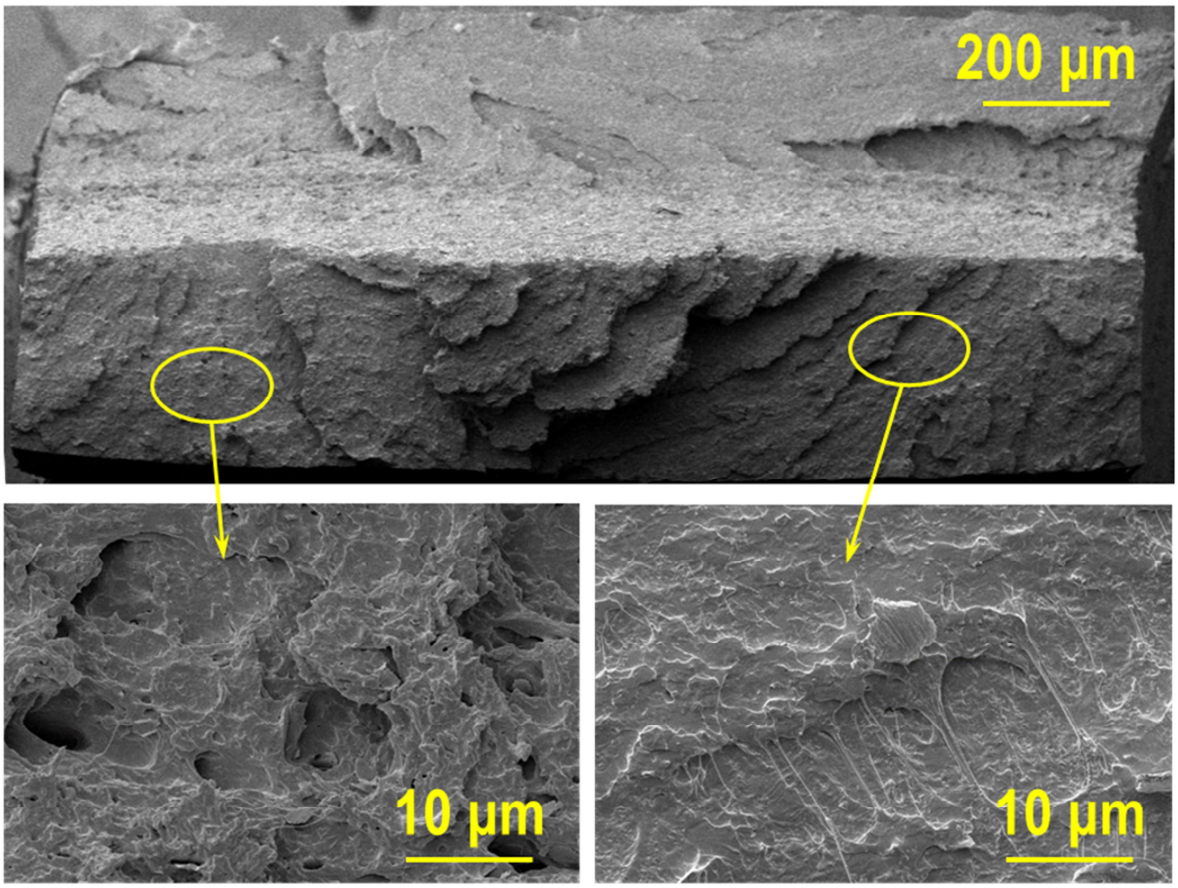

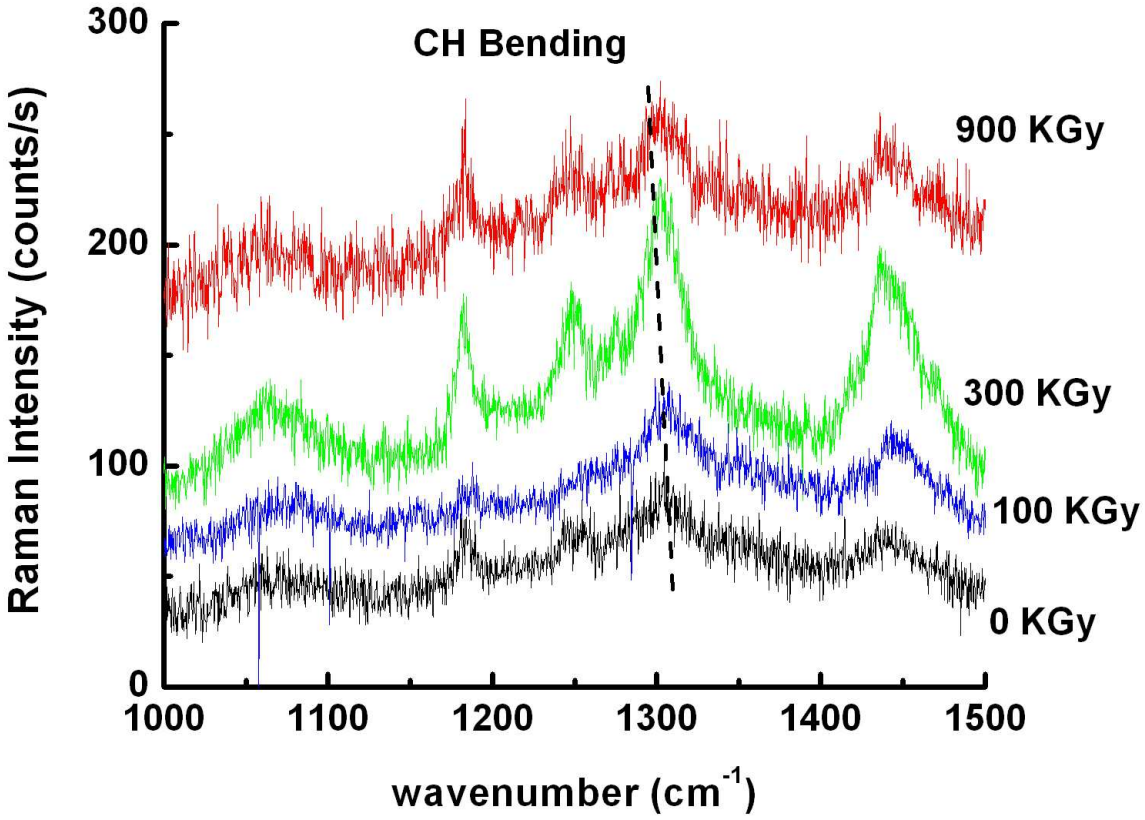

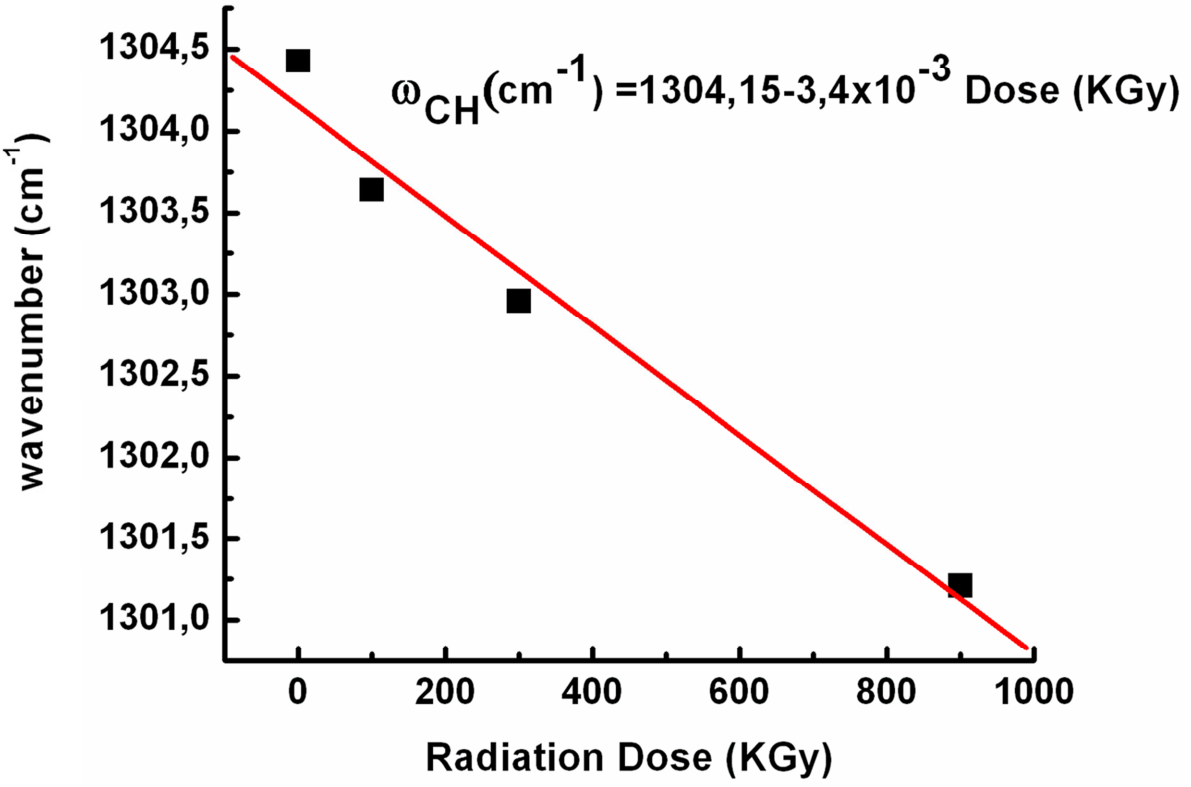

Highlights:

- Polyurethane exposed to high doses of X or gamma rays (20.5, 100, 300 and 900 kGy) or to neutron irradiation (fluence of $7.23 \cdot 10^{10}$ n / cm^2) has been studied.
- The evolution of strength, ductility and toughness was measured as a function of the dose.
- X and gamma rays negatively affect the mechanical properties. Statistics show that a threshold dose of 300 kGy must be overcome to trigger the damage process.
- Neutron irradiation produces slight changes in the mechanical properties.
- The SEM fractographic study fairly agrees with the mechanical outcomes.
- Raman spectroscopy shows that the band corresponding to the vibration of the C-H bending strongly correlates with the dose of exposure to electromagnetic radiation.