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Shape Memory Behavior of a Commercial Gamma-Irradiated Polycyclooctene

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Abstract: Gamma radiation process for modification of commercial polymers is a widely applied technique to promote new physical, chemical and mechanical properties. Gamma irradiation originates free radicals which can induce chain scission or crosslinking in the polymer backbone. The aim of this work is to research the structural, thermal and mechanical changes induced on a commercial polycyclooctene (PCO) when it is irradiated with a gamma source of ^{60}Co. After gamma irradiation, gel content was determined by Soxhlet extraction in cyclohexane, and thermal properties were evaluated before Soxhlet extraction by means of Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Finally, the shape memory properties were evaluated both qualitatively and quantitatively, the last one by Thermo-Mechanical Analysis (TMA).

Keywords: Gamma irradiation, Crosslinking, Thermo-Mechanical Analysis, Shape Memory behavior

1. Introduction

Shape memory polymers (SMPs) are those capable of recovering their original shape after having been deformed into a different one (temporary shape), i.e. they 'remember' the shape

they were given when processed (permanent shape). The shape memory effect can be induced under appropriate stimulus such as temperature [1,2].

The irradiation of polymeric materials with ionizing radiation, like gamma rays, leads to the formation of free radicals [3], which can produce crosslinking and/or scission of the macromolecular chains [4]. Different polymers have been crosslinked employing gamma rays, like polyethylene [5,6], polyamides [7] and poly(vinylidene fluoride) [8].

Under the controlled crosslinking process, polycyclooctene (PCO) has shown excellent shape memory properties [9]. Polycyclooctene has been previously crosslinked using a peroxide [10–12] and employing a gamma rays source [13,14], showing interesting properties.

Here we present the thermal behavior of a selection of polycylooctene samples irradiated at different dosages of gamma rays and we compare them with a non-radiated polycylooctene sample. Additionally, the shape memory behavior of the irradiated samples is analyzed, showing promising results.

2. Results and Discussion

The measurement of gel content by Soxhlet extraction is considered a simple way to determine the degree of crosslinking reached after the gamma irradiation process. The gel fraction (wt%) indicates the insoluble fraction of the irradiated PCO samples. The results are summarized in Table 1. The gel fraction is higher as the radiation dose increases. This increase in the gel content values may be attributed to the radiation crosslinking in the PCO chains.

Thermogravimetric analysis (TGA) provides quantitative information of the weight loss process. All PCO samples decompose in one main breakdown stage (Figure 1). The degradation temperatures (T_d) are listed in Table 1, and there are not significant differences between the samples.

DSC measurements were performed in order to know the transition temperature (T_{trans}) of the shape memory effect, which corresponds with melting temperature (Figure 2).

From the first scan, it appears that radiation has no pronounced influence on T_m, whereas in the second scan T_m decrease with increasing radiation dose. It is well known that during polymer irradiation, both chain scission and crosslinking processes occur, and they take place, primarily, in the amorphous region, while some may take place in the interphase between the crystalline and amorphous regions [15], so it is logic not to observe changes in melting temperature in the first heating. The diminution of this value in the second heating scan can be explained as follows: the samples are recrystallized in the presence of the crosslinks formed in the irradiation process, which act as defect centres, restricting chain mobility of PCO chains, so T_m diminishes. The degree of crystallinity thus decreases with increased density of crosslinks due to more restricted mobility and conformational rearrangement of polymeric chains to form crystals.

The shape memory behavior of the samples has been studied both qualitatively and quantitatively.

In Figure 3 it can be observed the qualitatively studio for PCO-25 sample, whereas Figure 4 shows the same procedure for PCO-200. Both samples recover the original shape from an elbow-shaped temporary state, but in the case of the sample irradiated at 25 kGy this recovery is not total.

Thermomechanical Analysis was performed in order to quantify the shape memory behavior. The results are represented in Figure 5. Looking at Figure 5, recovery ratios near 100% can be

appreciate (at the end of the experiment, the length of the samples are similar to the initial ones). This result to PCO-25 seems to be in discrepancy with the qualitatively analysis (Figure 3), but it is necessary to take into account that the thermo-mechanical cycle is completely different considering the different deformation mode and thermal treatment from the qualitative analysis made employing a hot and a cold bath, and a digital camera.

Table 1. Gel fraction, crystallinity values and characteristic temperatures for the studied samples.

Sample	Gel Fraction (wt%)	T_d (ºC)	T_{m1} (ºC)	T_c (ºC)	T_{m2} (ºC)	Crystallinity (%)
PCO-0	0	461.8	60.7	37.0	57.5	30.3
PCO-25	21.3	463.7	60.0	34.1	57.6	30.3
PCO-100	86.9	463.4	60.1	30.0	54.6	25.9
PCO-200	94.6	458.1	59.6	27.7	52.5	22.8

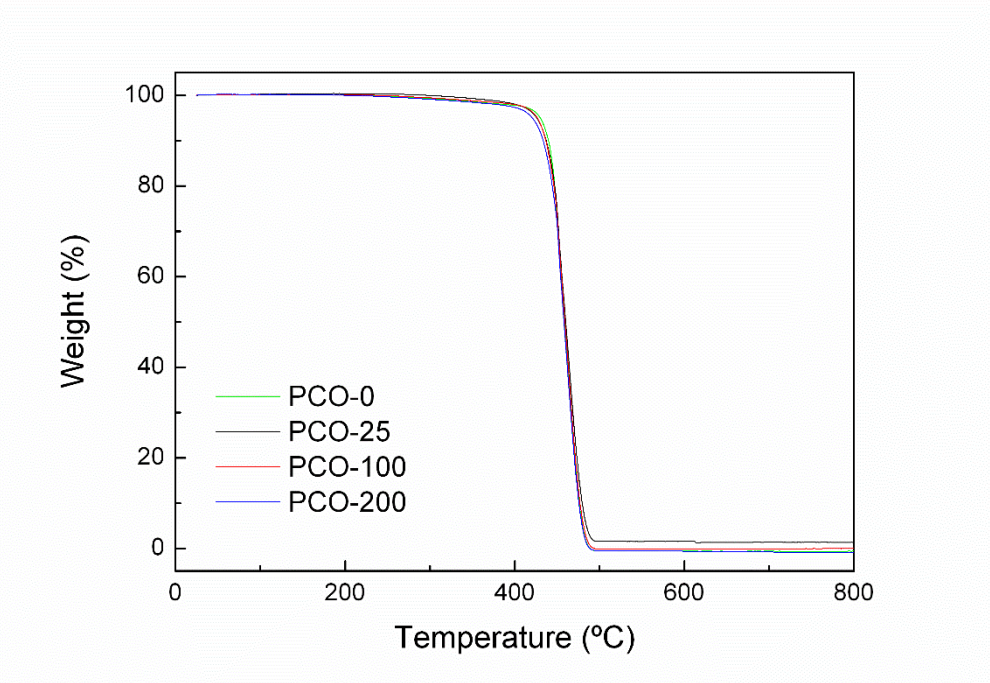

Figure 1. TGA curves for the studied PCO samples.

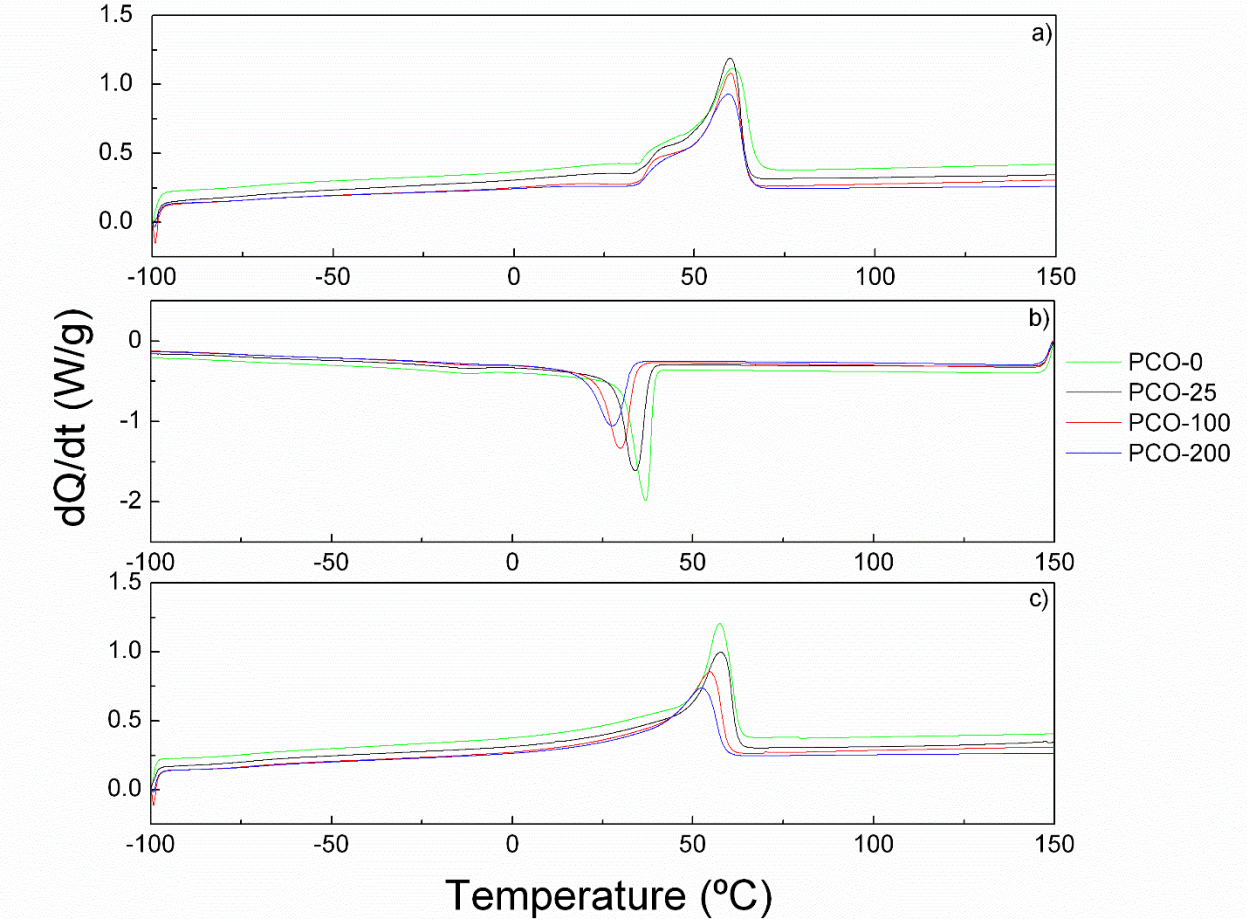

Figure 2. DSC curves for PCO samples: a) first heating, b) cooling and c) second heating scan.

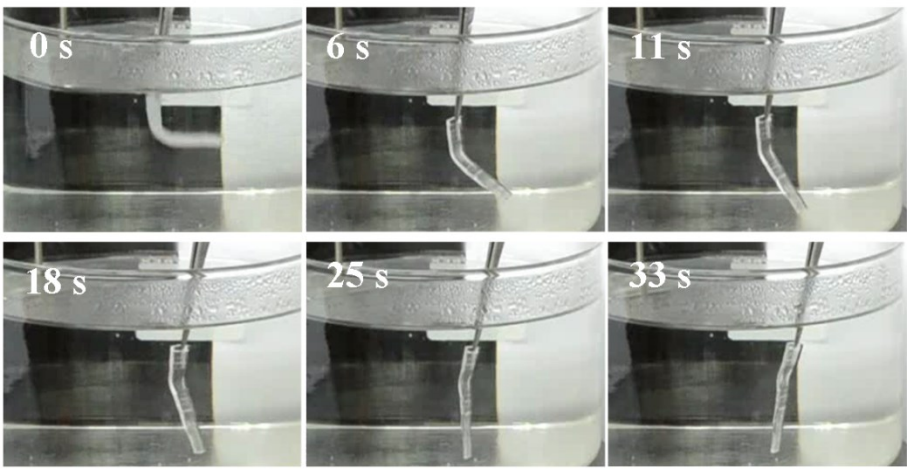

Figure 3. Shape memory recovery of elbow-shaped bent strip for 25 kGy irradiated PCO sample.

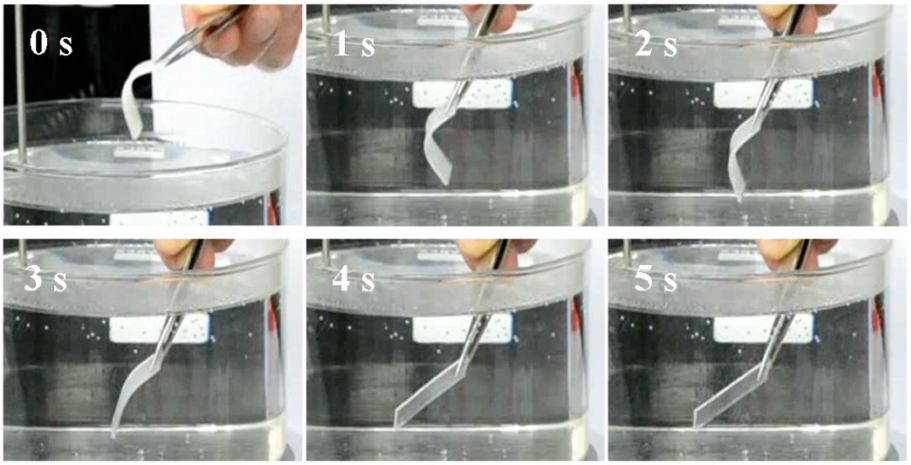

Figure 4. Shape memory recovery of elbow-shaped bent strip for 200 kGy irradiated PCO sample.

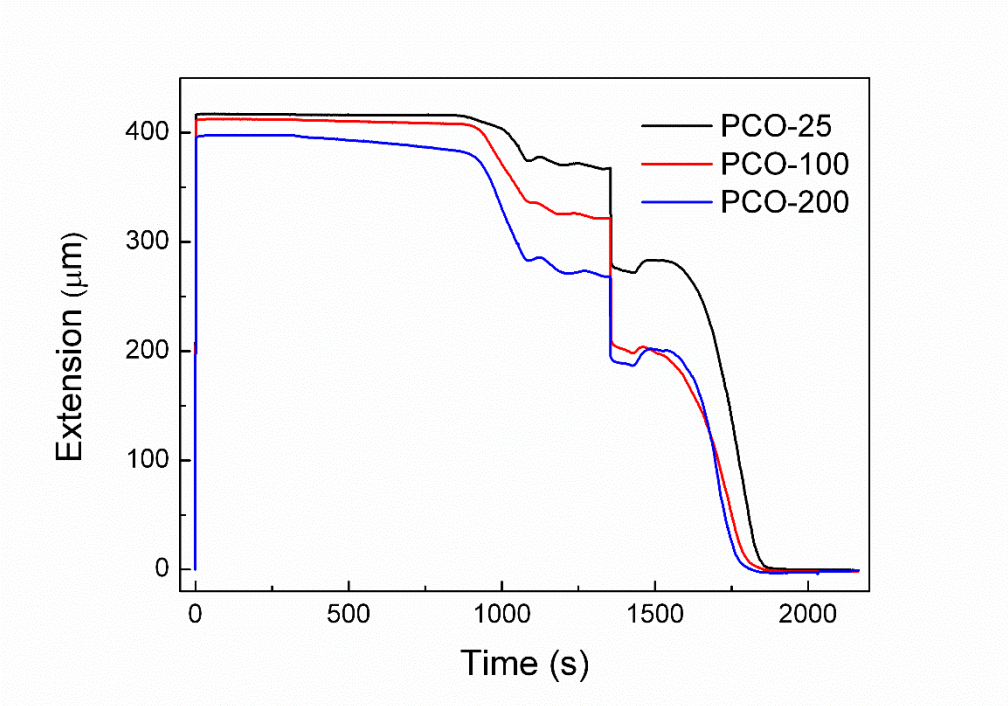

Figure 5. Thermo-mechanical cycle for PCO irradiated samples.

3. Materials and Methods

Polycyclooctene (PCO) Vestenamer® 8012 sheets were made by compression molding employing a hydraulic press with thermostatically controlled platens. PCO sheets were irradiated by gamma rays in a ^{60}Co radiation facility (NÁYADE Irradiation Plant of CIEMAT, Madrid, Spain) at the dosages of 25, 100 and 200 kGy [14].

The gel content of PCO samples was determined gravimetrically using 10 Soxhlet extraction cycles with boiling cyclohexane as solvent. After extraction, the samples were washed and vacuum dried at 50ºC to constant weight. The gel fraction was calculated using the following equation, where W_0 is the initial weight of sample and W_1 is the weight of sample after extraction.

$$gel\ fraction\ (wt\%) = \left({}^{W_1}/_{W_0}\right) \times 100$$

Thermal stability of the samples was evaluated by Thermogravimetric Analysis with a Mettler Toledo TGA/SDTA 851e thermobalance. The measurements were carried out from 25 to 800ºC with a heating rate of 10ºC·min^{-1} under nitrogen atmosphere (Figure 1).

Thermal properties of all samples were measured by Differential Scanning Calorimetry (DSC 822e from Mettler Toledo) to identify thermal actuation temperatures. The transition temperature of shape memory effect (T_{trans}) was defined from melting temperature measured in the second heating cycle (T_{m2}). Employing a constant nitrogen flow (50 mL·min^{-1}), samples were heated from −100 to 150ºC at a rate of 10ºC·min^{-1}, followed by a cooling scan from 150 to −100ºC at a rate of −10ºC·min^{-1}. Subsequently, a second heating scan to 150ºC was conducted at the same heating rate (Figure 2). The crystallinity of the samples was calculated using the next equation, employing the melting temperature in the second heating scan for each sample, where the enthalpy of a 100% crystalline polycyclooctene was 230 J·g^{-1} [16].

$$\%\ cryst = \left\{{}^{\Delta H_{m2}\ sample}/_{\Delta H_m(PCO)}\right\} \times 100$$

Thermally-induced shape memory behavior of irradiated PCO samples was qualitatively evaluated by digitally monitoring the shape recovery process. Rectangular strip samples were deformed in elbow-shaped strips at temperatures 10ºC above its transition temperature of shape memory effect. The temporary shape was fixed cooling down the temperature 20ºC below T_{trans}, and finally, the samples were heated-up above the transition temperature, so the thermal-induced recovery process was observed (Figures 3 and 4).

The quantitative evaluation of the shape memory behavior was performed using thermomechanical analysis (TMA). For that, samples shaped as strips with a cross-section area of 4 mm x 1.5 mm and initial clamps distance of 20 mm was employed. Taking into account the melting temperatures of the samples (Table 1), we thought appropriately to perform the thermo-mechanical experiments in the temperature range of 30-80ºC [17]. The analysis were conducted on a Mettler Toledo DMA-1 at a heating rate of 4ºC min^{-1}, recording the increase of the sample length as a function of temperature (Figure 5).

4. Conclusions

A commercial polycyclooctene (PCO) was irradiated with a gamma source of ^{60}Co at different doses (25-200 kGy). Soxhlet extraction allowed to measure the gel fraction for each sample. This insoluble fraction of each irradiated PCO sample is directly related to the degree of crosslinking reached for each sample in the radiation process, and it is higher as the radiation dose increases.

Thermal properties were evaluated by means of TGA and DSC, showing that the thermal stability of all PCO samples is quite similar independently of radiation dose.

The investigation of the thermal properties by DSC shows minor changes in the melting temperature with irradiation doses in the first heating scan (T_{m1}), which could be attributed to the immobilization of the generated free radicals in the crystalline region with hindered chain mobility. However, for the second heating scan, a decrease in T_{m2} with the increasing radiation dose was observed. During the recrystallization process, crosslinks between polymer chains act as defect centers, which restrict chain mobility of PCO chains and, therefore, the T_m values determined from the second heating scan are lower.

Finally, shape memory behavior of irradiated PCO samples was qualitatively and quantitatively evaluated. Except for the sample irradiated at 25 kGy, where the recoverability is not total, the qualitative evaluation demonstrate promoted shape memory response for the irradiated samples. At the same time, the quantitative analysis using TMA show that all the irradiated samples are characterized by recovery ratios near 100%.

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Author Contributions

Nuria García-Huete conducted the experimental work and the processing of data and wrote the paper. José María Cuevas, José Manuel Laza, José Luis Vilas and Luis Manuel León contributed to discussion and interpretation of results.

Conflicts of Interest

The authors declare no conflict of interest.

References and Notes

1. Liu, C.; Chun, S. B.; Mather, P. T.; Zheng, L.; Haley, E. H.; Coughlin, E. B. Chemically cross-linked polycyclooctene: synthesis, characterization, and shape memory behavior. *Macromolecules* **2002**, *35*, 9868–9874.

2. Lendlein, A.; Kelch, S. Shape-memory polymers. *Angew. Chemie Int. Ed.* **2002**, *41*, 2034–2057.

3. Chmielewski, A. G.; Haji-Saeid, M.; Ahmed, S. Progress in radiation processing of polymers. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **2005**, *236*, 44–54.

4. Zahran, A. R. R.; Kandeil, A. Y.; Higazy, A. A.; Kassem, M. E. Ultrasonic and thermal properties of γ-irradiated low-density polyethylene. *J. Appl. Polym. Sci.* **1993**, *49*, 1291–1297.

5. Basfar, A. A. Flammability of radiation cross-linked low density polyethylene as an insulating material for wire and cable. *Radiat. Phys. Chem.* **2002**, *63*, 505–508.

6. Vachon, C.; Gendron, R. Effect of gamma-irradiation on the foaming behavior of ethylene-co-octene polymers. *Radiat. Phys. Chem.* **2003**, *66*, 415–425.

7. Feng, W.; Hu, F. M.; Yuan, L. H.; Zhou, Y.; Zhou, Y. Y. Radiation crosslinking of polyamide 610. *Radiat. Phys. Chem.* **2002**, *63*, 493–496.

8. Medeiros, A. S.; Gual, M. R.; Pereira, C.; Faria, L. O. Thermal analysis for study of the gamma radiation effects in poly(vinylidene fluoride). *Radiat. Phys. Chem.* **2015**.

9. Alonso-Villanueva, J.; Cuevas, J. M.; Laza, J. M.; Vilas, J. L.; León, L. M. Synthesis of poly(cyclooctene) by ring-opening metathesis polymerization: Characterization and shape memory properties. *J. Appl. Polym. Sci.* **2010**, *115*, 2440–2447.

10. Cuevas, J. M.; Laza, J. M.; Rubio, R.; German, L.; Vilas, J. L.; León, L. M. Development and characterization of semi-crystalline polyalkenamer based shape memory polymers. *Smart Mater. Struct.* **2011**, *20*, 035003.

11. Cuevas, J. M.; Rubio, R.; Laza, J. M.; Vilas, J. L.; Rodriguez, M.; León, L. M. Shape memory composites based on glass-fibre-reinforced poly(ethylene)-like polymers. *Smart Mater. Struct.* **2012**, *21*, 035004.

12. Cuevas, J. M.; Rubio, R.; German, L.; Laza, J. M.; Vilas, J. L.; Rodriguez, M.; Leon, L. M. Triple-shape memory effect of covalently

crosslinked polyalkenamer based semicrystalline polymer blends. *Soft Matter* **2012**, *8*, 4928–4935.
13. Abdel-Aziz, M. M.; Basfar, A. A. Aging of ethylene-propylene diene rubber (EPDM) vulcanized by γ-radiation. *Polym. Test.* **2000**, *19*, 591–602.
14. García-Huete, N.; Laza, J. M.; Cuevas, J. M.; Vilas, J. L.; Bilbao, E.; León, L. M. Study of the effect of gamma irradiation on a commercial polycyclooctene I. Thermal and mechanical properties. *Radiat. Phys. Chem.* **2014**, *102*, 108–116.
15. Luo, S.; Netravali, A. N. Effect of 60Co γ-radiation on the properties of poly (hydroxybutyrate- co- hydroxyvalerate). *J. Appl. Polym. Sci.* **1999**, *73*, 1059–1067.
16. Schneider, W. A.; Müller, M. F. Crystallinity of trans-polyoctenamer: characterization and influence of sample history. *J. Mol. Catal.* **1988**, *46*, 395–403.
17. Axpe, E.; García-Huete, N.; Cuevas, J. M.; Ribeiro, C.; Mérida, D.; Laza, J. M.; García, J. Á.; Vilas, J. L.; Lanceros-Méndez, S.; Plazaola, F.; León, L. M. Connecting free volume with shape memory properties in noncytotoxic gamma-irradiated polycyclooctene. *J. Polym. Sci. Part B Polym. Phys.* **2015**, *53*, 1080–1088.