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EXECUTIVE SUMMARY OF THE THESIS

Radiation Effects on Candidate Self-Healing Polymers for Space Applications

TESI MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY – INGEGNERIA DEI MATERIALI E DELLE NANOTECNOLOGIE

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1. Introduction

The emerging challenges and the increasing duration of space exploration missions are prompting scientists to take more into consideration the research and development of self-healing materials for practical applications, such as inflatable structures and space suits. These materials would have the potential to extend the lifetime of components, minimizing the need for on-site repairs and improving safety for crew members. Limiting their durability and feasibility is the rapid deterioration of structures due to the extreme conditions of the space environment, which includes the presence of micrometeorites and orbital debris, atomic oxygen, vacuum, high radiation exposure and extreme temperature fluctuations.

The main purpose of this master's thesis is to assess the change in the healing performance of candidate self-healing polymers for space applications, as a consequence of exposure to γ-radiation through a simulated space environment.

2. Materials tested

The materials tested and reported in this thesis study are: four different poly(urea-urethane)s (PUUs) and the Arkema's Reverlink® HR. Those materials were supplied by the European Space Agency (ESA).

Poly(urea-urethane) is a type of polyurethane (PU) block copolymer with two different types of N-H bonds in the urethane and urea linkages. The healing mechanism involves the formation of two distinct chemical bonds: a reversible supramolecular noncovalent interaction, performed by hydrogen bonding, and a reversible covalent bond of disulfide bridge. Four different PUUs samples with fixed disulphide content but different crosslinking densities were analyzed, created by varying the trifunctional:difunctional pre-polymer ratio from 100:0 to 70:30 [1].

Arkema's Reverlink® HR is a supramolecular polymer containing both weak reversible supramolecular hydrogen bonds, to which the intrinsic self-healing mechanism is attributed, and strong irreversible covalent bonds (50:50 mol%).

In order to simulate the effects of the prolonged exposure to γ-radiation in a space environment, two batches of samples were irradiated with a total ionizing dose of 100 and 500 krad respectively. The irradiation tests were performed in air with the Co60 facility at ESA-ESTEC.

3. Test methods and results

3.1. ATR-FTIR, DSC and TGA characterization

Samples were characterized by means of ATR-FTIR spectroscopy and DSC and TGA analysis, in order to detect possible differences at the chemical and molecular level due to the different radiation doses absorbed. Figure 1 and Figure 2 show respectively examples of ATR-FTIR spectra and DSC comparison between blanks and irradiated samples [2].

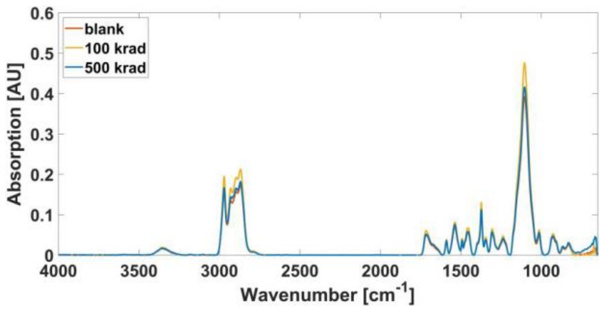


Figure 1: ATR-FTIR spectra comparison of blank and irradiated PUU 80.

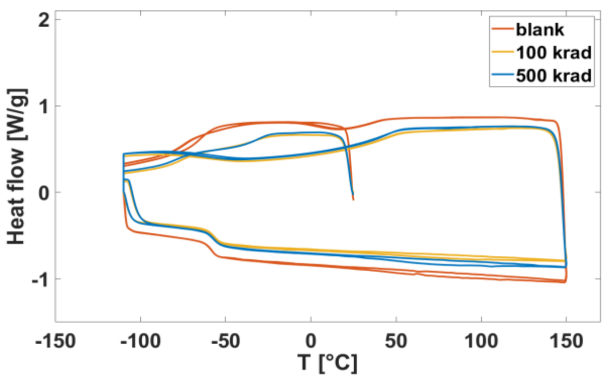


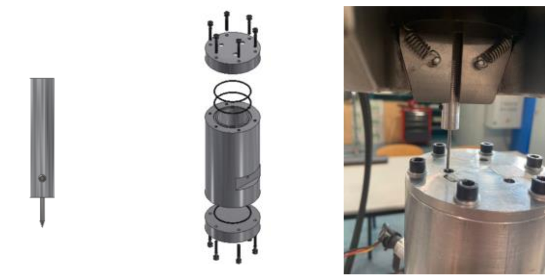
Figure 2: DSC results comparison of blank and irradiated PUU 100.

After comparing the results obtained from the characterization done for blanks and for the two irradiated sets, no significant differences due to irradiation emerged for the two types of polymers tested.

3.2. Puncture test

3.2.1 Working principle

The purpose of this test is to simulate the perforation of the material due to direct contact with a micrometeorite travelling in space, and subsequently evaluate the self-healing response of the material following puncture. The two main apparatus of the device can be seen in Figure 3 (a) and (b). Air is injected into the cylindrical vessel at a pressure of 0.3 bar. It is then closed using a sealing ring perforated with holes, in correspondence of which samples are placed. The puncture takes place at these holes using a 2 mm diameter puncture needle attached on the puncture probe, perforating the sample with a velocity of 8.467 mm/s (Figure 3 (c)).



(a) puncture probe (b) cylindrical vessel (c) puncture event

Figure 3: Main device's apparatus scheme and puncture event picture.

The air flow rate exiting the cylinder is monitored during the test. It will be maximum at the puncture event, when the hole is formed, and will go to zero after a transient following the healing of the material.

After each successful puncture test, a leakage test was performed on the same sample. This test consisted of a gradual increase of pressure inside the cylinder, going from 0.3 to 0.8 bar. The aim was to assess whether the flow rate going to a null value after the puncture test was due to a simple elastic recovery of the sample or due to an actual repair of the hole.

3.2.2 Results

The maximum and the minimum flow rate, Q_{max} and Q_{min}, the time in between the two Δt and the total volume lost V_{leak} were considered as healing performance indicators. The V_{leak} parameter is

considered as the most important parameter since the material, in order to be considered suitable for space applications, must lose as less air volume as possible. This requirement is critical for the safety of the crew, to minimize oxygen loss, and for the inflatable structure, to maintain its rigidity.
The averaged tests' results, in terms of the chosen healing performance indicators, for irradiated and blank samples, are listed in Table 1. It is shown that all PUUs, both irradiated and non-irradiated, come to repair with very low air volume lost during the test and a low value of maximum flow rate. The only exceptions are PUU 90 blank and PUU 100 irradiated by 500 krad dose, but still showing a very low value of Q_{min}. In contrast, the results are worse for Reverlink®, for which both Q_{max} and V_{leak} are much higher. In addition, for 500 krad radiation dose it is not able to fully repair itself. Every leakage test performed on successful puncture tests exceeded.

Sample type	Q_{max} $[l/min]$	Q_{min} $[l/min]$	Δt $[s]$	$V_{leak}[l]$
PUU 70				
Blank	2.0571	0	104.33	0.0522
100 krad	1.9865	0	6.14	0.0053
500 krad	2.1881	0	34.63	0.0136
PUU 80				
Blank	2.2541	0	10.95	0.0143
100 krad	1.8762	0	5.34	0.0056
500 krad	1.9441	0	9.76	0.0093
PUU 90				
Blank	2.2153	0.003	162.48	0.0542
100 krad	2.2094	0	4.81	0.0119
500 krad	2.1378	0	48.37	0.0212
PUU 100				
Blank	2.0026	0	59.35	0.0196
100 krad	1.8961	0	7.07	0.0060
500 krad	1.9720	0.0058	28.87	0.0347
Reverlink®				
Blank	3.4610	0.0014	234.96	0.3214
100 krad	5.9902	0	101.88	0.3461
500 krad	3.4774	0.0748	452.38	0.7480

Table 1: Puncture test results comparison for blank and irradiated samples.

Comparing the results for irradiated and blank samples for PUUs an unexpected improvement in self-healing performance, following irradiation, is evident. Looking at all the considered parameters, especially V_{leak}, this improvement is very pronounced for polymers irradiated at 100 krad dose, while it is less for those irradiated at 500 krad dose. The opposite is the case of Reverlink®, for which the self-healing performance worsens by increasing the radiation dose, going so far as to be unable to repair itself at a dose of 500 krad.

An example of comparison of flow rate curves between irradiated and blank samples is shown in Figure 4.

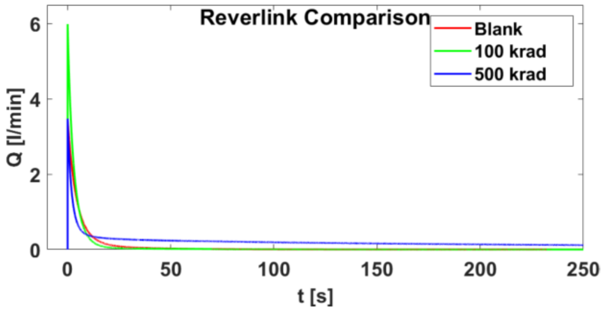


Figure 4: Reverlink® flow rate comparison between blank and irradiated.

4. Modeling

A viscoelastic model was developed for the analysis of the polymers' viscoelastic properties and the assessment of their changes due to irradiation. The model is based on the main idea that the puncture test can be seen as a relaxation test, in which the air flow rate exiting the punctured sample is directly proportional to the radius of the hole created through the equation [3]:

$$Q(t) = \frac{\dot{m}(t)}{\rho_a} \quad (1)$$

Where $\dot{m}(t)$ represents the mass flow rate through the hole:

$$\dot{m}(t) = C_d \cdot A_h(t) \cdot \psi \cdot p_0 \cdot \sqrt{\frac{2}{R_a \cdot T_0}} \quad (2)$$

C_d is the discharge coefficient, p_0 is the absolute pressure inside the cylindrical vessel, T_0 is the absolute temperature, R_a is the gas constant of air and ψ is the pressure dependent outflow function. $A_h(t)$ is the area of the hole through which the air flows, in mm^2, assumed to be always circular during time:

$$A_h(t) = \pi \cdot r^2(t) \quad (3)$$

By handling these equations, the trend of the hole radius $r(t)$ after the puncturing can be obtained. During puncturing, namely during the time interval when the puncturing needle is inside the sample, the radius of the hole equals $r_{probe} = 1\,mm$. As it exits the sample, the radius decreases instantaneously to a value r_0 as a result of the elastic strain recovery, then continuing to decrease due to viscoelastic strain recovery according to the $r(t)$ trend obtained from Equations 1, 2 and 3.

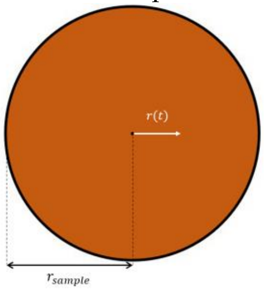


Figure 5: Approximation of the polymer sample as a 2D disk.

The overall radius trend can be related to the strain trend experienced by the sample during the test, approximating its shape to a 2D disk of radius $r_{sample} = 10\ mm$ and assuming that puncturing occurs exactly in its center (Figure 5).
The strain is, for the sake of simplicity, considered positive:

$$\varepsilon(t) = \frac{r(t)}{r_{sample}} \tag{4}$$

A scheme of the strain trend over time is shown in Figure 6.

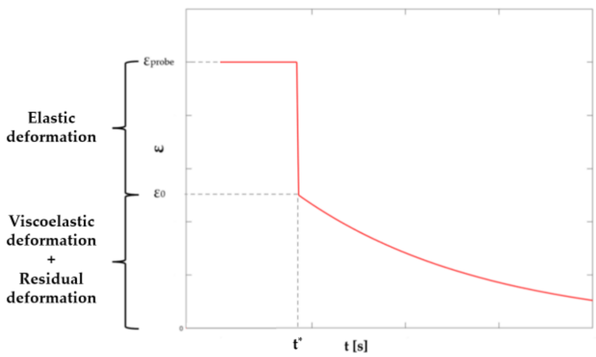


Figure 6: Scheme of the hole strain trend during the test.

As a consequence of the created model, the value of ε_0 is directly related to the value of Q_{max}. In fact, the greater the value of Q_{max}, the greater will be the corresponding value of r_0, so ε_0, and consequently the lower will be the percentage of elastic deformation experienced by the polymer.
Next, the three-element Zener model in Kelvin-Voigt representation was chosen to represent the viscoelastic behavior of polymers.

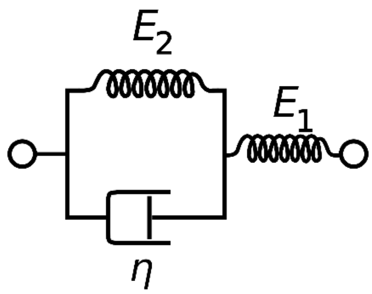


Figure 7: Zener model in Kelvin-Voigt representation.

Considering the constitutive equation and the actual boundary conditions on strain during the test, the Zener model's strain trend for the system under investigation is as follows:

$$\varepsilon(t) = \varepsilon_0 \cdot \exp\left(-\frac{E_2 \cdot t}{\eta}\right) = \varepsilon_0 \cdot \exp\left(-\frac{t}{\tau}\right) \tag{5}$$

Where τ is the relaxation time:

$$\tau = \frac{\eta}{E_2} \tag{6}$$

4.1. Fitting and results

The strain trends for the polymers tested, obtained from Eq 4, were fitted with the resulting strain trend from Zener model (Equation 5) through the Matlab Fitting Tool, having τ as the only variable parameter with constrains:

$$10^5 < \tau < 10 \qquad s$$

derived from the constraints considered for E_2 and η:

$$10^5 < E_2 < 10^9 \qquad MPa$$
$$10^4 < \eta < 10^8 \qquad MPa/s$$

Given these conditions, the software returns the value of τ for the best fitting. The values of E_1, E_2 and η for the polymers are obtained considering the boundary conditions on hole's deformation during the test. Figure 8 show an example of fitting.

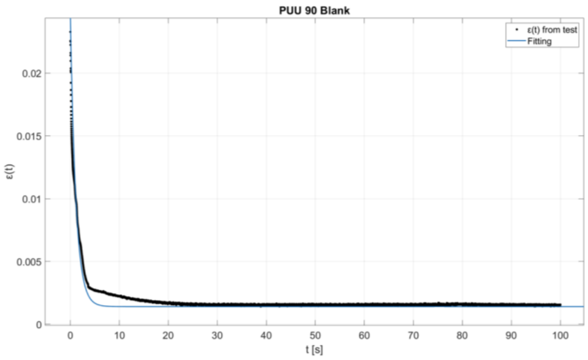


Figure 8: Fitting for PUU 90 Blank.

Table 2 illustrates the values of E_1, E_2, η and τ resulting from the proposed viscoelastic model, together with the elastic and viscoelastic deformation percentage.

Polymer	E_1 $[MPa]$	E_2 $[MPa]$	η $[MPa \cdot s]$	τ $[s^{-1}]$	Elastic strain %	Viscoelastic strain %
			PUU 70			
Blank	4.03	13.95	10.93	0.783	77.56	22.44
100 krad	10.91	38.90	10.10	0.260	78.09	21.91
500 krad	4.75	15.83	10.81	0.683	76.87	23.13
			PUU 80			
Blank	4.88	15.98	10.80	0.676	76.60	23.40
100 krad	8.14	29.90	10.19	0.341	78.63	21.37
500 krad	6.36	22.83	10.38	0.455	78.23	21.77
			PUU 90			
Blank	2.80	9.65	11.96	1.24	76.72	22.27
100 krad	4.69	15.44	10.80	0.699	76.75	23.25
500 krad	3.15	10.67	11.27	1.057	77.16	22.84
			PUU 100			
Blank	4.23	15.14	11.01	0.727	77.88	21.77
100 krad	7.88	28.78	10.24	0.356	78.48	21.52
500 krad	7.45	26.40	10.27	0.389	78.04	20.93
			Reverlink®			
Blank	0.56	1.39	13.89	10	70.90	28.68
100 krad	1.34	2.26	15.01	6.650	62.70	37.30
500 krad	0.98	2.73	15.37	5.640	70.85	25.45

Table 2: Viscoelastic parameters comparison resulting from the model.

The determination of elastic and viscoelastic deformation is based on the corresponding value of ε_0 (Figure 6).

The parameter τ is directly related to how quickly the material recovers the viscoelastic deformation, so the decay rate, and it is related to the value of viscosity η. The higher the τ value, the slower the recovery and presumably the greater is the volume of air lost (which, however, also depends on the actual total repair of the material).

It can be seen that Reverlink® is much more viscous than PUUs, thus justifying the worse self-healing performance.

By comparing the values resulting from the model for irradiated and blank samples, an increase in stiffness due to irradiation can be seen for both types of polymers. This increase of stiffness tends to be greater for 100 krad dose than 500 krad dose. Considering viscosity instead, we have an opposite effect for PUUs and Reverlink®. PUUs experience a decrease in viscosity due to irradiation, again greater for the 100 krad dose than for 500 krad. The effect on Reverlink®, on the other hand, is opposite, with an increase of viscosity as the radiation dose suffered increases.

The τ value decreases for both polymers upon irradiation, while the percentage of elastic strain remains essentially unchanged (except in the case of Reverlink® at a dose of 100 krad, in which it decreases).

5. Final considerations and conclusions

The ionizing radiation causes chemical degradation of polymers, which may result in the formation of highly reactive species such as free neutral radicals, cationic and anionic ions or excited molecules. Molecular modifications mainly consist in molecular cross-linking or chain scission. Crosslinking reactions form new C-C covalent bonds between adjacent molecular chains, forming a three-dimensional network and increasing in this way the molecular weight, thus reducing chain mobility. Chain scission, instead, results in a decrease of the molecular weight of the polymer and so in an increase of chain mobility. Consequently, the higher is the chain mobility, the better is the self-healing performance of the polymer and vice-versa. Those phenomena coexist during ionization, the prevalence of one over the other depends on several factors such as the morphology of the polymer, the irradiation environment and the initial molecular structure [4].

The reason for the improvement of self-healing performance for PUUs after irradiation lies on the bond nature of PUUs. Indeed, they contain a high content of reversible non-covalent hydrogen bonds and a very lower constant content of covalent disulphide bonds. As the radiation dose experienced by the polymer increases, the most prevalent mechanism in polymers where hydrogen bonds are present is chain scissioning [5], causing an increase in chain mobility, thus a faster strain recovery and consequently a better self-healing performance. A decrease in viscosity due to this phenomenon is indeed shown through the considered model (Table 2). The scissioning mechanism is also responsible for an increase in the degree of crystallinity of the polymer, with a

consequent increase in stiffness. No particular trend towards increasing trifunctional:difunctional ratio for PUUs is evident from the results. PUU 90 tends to be the worst performing one, while PUU 80 is the best performing one.
Reverlink®, on the other hand, exhibits the opposite behavior, thus worsening the self-healing efficiency with increasing radiation dose. The reason for this can again be found in the nature of the polymer bonds. They consist of weak hydrogen bonds and strong irreversible covalent bonds (50:50 mol%). As introduced before, polymers where hydrogen bonds are present, especially supramolecular polymers, undergo mostly chain scission due to gamma irradiation [5], while the regions of the polymer with irreversible covalent bonds undergo a crosslinking mechanism. Since in Reverlink® the latter are much stronger than hydrogen bonds, the effects of crosslinking will prevail. For this reason, overall, the polymer undergoes an increase in molecular weight and thus a decrease in chain mobility. The viscoelastic model considered indeed shows an increase in viscosity and stiffness of the polymer. By increasing the radiation dose, the crosslinking mechanism becomes so important that hinders the self-healing process, which is actually attributable to hydrogen bonds. This is why the puncture test results show a missed repair of the polymer at 500 krad radiation dose.
However, for both PUUs and Reverlink®, slight changes in material behavior due to irradiation are observable from the test results. Indeed, taking into account the characterization performed on them, no significant variations are evident from a chemical and molecular point of view.

5.1. Conclusions and future developments

For PUUs, the results of the comparison show the unexpected result of an improvement in self-healing performance. This, taking into account the parameters considered in the proposed viscoelastic model, was attributed to a chain scission mechanism due to irradiation. In addition, the results did not show a clear performance trend when varying the crosslinking density. On the other hand, from the results obtained, Reverlink® showed a deterioration in self-healing efficiency due to irradiation, not repairing completely for a radiation dose of 500 krad. This effect was attributed to a crosslinking mechanism prevailing over chain scissioning.
Overall, the results of the test comparison show that, among the two types of polymers tested, PUUs clearly have better self-healing properties and a lower susceptibility to the radiation doses considered than Reverlink®
Finally, at the end of this study, it can be concluded that PUUs show very good results in terms of self-healing performance due to irradiation, but further tests should be carried out to assess the effects of different irradiation rates, radiation doses and smaller thicknesses. In order to establish whether PUUs might really be candidates for space applications, such as inflatable habitats and spacesuits, it would be necessary to evaluate the effects of the other damaging agents present in the space environment (UV, thermal solicitations, ATOX and higher radiation doses), ageing and humidity.

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