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SELF-HEALING MULTILAYER COMPOSITES AND NANOCOMPOSITES FOR SPACE APPLICATIONS: A STUDY ON DAMAGE RECOVERY PERFORMANCE AFTER SIMULATED SPACE RADIATION EXPOSURE

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Abstract

In recent decades, the possibility of integrating self-healing materials into inflatable and deployable space structures has drawn the attention of the scientific community. This solution would make human activity in space safer and increase spacecraft operational life and autonomy. Nevertheless, the action of space environment may deteriorate these materials.

The presented work analyzes the autonomous repair ability of candidate self-healing polymers, used as nanocomposite matrices or coupled with an elastomer or aramid fabric into a multilayer. Self-healing is evaluated through in-situ flow rate measurements after puncture damage. In the multilayer case, the tests are then repeated on gamma-ray irradiated samples to study the variation of self-repairing and functional properties after exposure to simulated space radiation.

Results show higher repair ability in systems with lower viscous response, and decreased healing performance in the irradiated samples, hence requiring a further analysis of the effects of space environment on the presented materials.

Keywords: self-healing polymers; multilayer; nanocomposites; space radiation; multifunctionality

1. Introduction

Inflatable and deployable structures have recently been considered for space applications, as they would ensure reduced mass and launch cost due to their light weight and high packing efficiency. Nevertheless, their structural integrity might be compromised by environmental factors such as vacuum, atomic oxygen, radiation, and micrometeoroids and orbital debris (MMOD). In particular, impacts with MMOD could generate punctures and cuts leading to depressurization of these structures, which would be a significant issue for long-term crewed missions. The integration of self-healing polymers into inflatable structures seems a promising solution to enhance the duration and safety of spacecraft for future missions, but these materials could themselves significantly change their properties under the action of space environment. As an example, they could undergo degradation due to their exposure to ionizing radiation from Galactic Cosmic Rays (GCR), Solar Particle Events (SPE) and Van Allen Belts (1). These aspects must hence be considered to design and characterize novel solutions for future space missions (2,3).

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The aim of the here presented work is to experimentally characterize the self-healing performance of polyurea-urethanes and a supramolecular polymer with intrinsic autonomic self-healing properties, and to assess their possible applicability to space. This research focuses on puncture tests, as they best represent MMOD impacts, analyzing their effect on different specimen configurations (4). Multilayer and nanocomposite samples are investigated alongside reference neat polymer specimens. After the initial puncture tests, some of the promising specimens are exposed to 100 Gy radiation doses before being tested again. A comparison is then made between pre and post irradiation results, to assess the possible changes of healing performance after exposure to radiation.

2. Materials and experimental setup

2.1 Self-healing polymers

Four poly(urea-urethane)s (PUUs) with similar formulation and fixed disulphide content but different crosslinking densities are analyzed (Table 1). They are obtained from different combinations of trifunctional and difunctional isocyanate-terminated pre-polymers PU-6000 and PU-4000, organized into networks connected by aromatic disulphides linkages and containing urea related H-bonds (5). These pre-polymers can be synthesized trough interaction of poly(propylene glycol) (PPG) and isophorone diisocyanate (IPDI) in the presence of the dibutyltin dilaurate (DBTDL) catalyst (6).

Table 1 : PUUs formulations and basic properties (5).

Sample	Composition [wt%]			ν [10^{-4} mol/cm^3]	T_g [°C]
	PU-6000	PU-4000	Linker		
PUU 100	93.8	0	6.2	2.35	-58.8
PUU 90	84.4	9.4	6.2	2.05	-59
PUU 80	75.1	18.7	6.2	1.77	-59.4
PUU 70	65.7	28.1	6.2	1.50	-60.1

Reverlink® HR contains both covalent bonds and supramolecular hydrogen-bonding crosslinks (50:50 mol%). It is obtained from the combination of supramolecular pre-polymer SP-50, diglycidyl ether of bisphenol A (DGEBA) resin and 2-Methyl Imidazole (2-MI) catalyst, with nominal proportions reported in Table 2 (7,8). The non-cured material is heated to 90 °C, poured into a Teflon® mold and then cured at temperatures in the 120-150 °C range. Its glass transition temperature is between 5 °C and 15 °C (9,10).

Table 2 : Self-healing element nominal components (7).

Component	SP-50	DGEBA	2-MI
Mass [g]	23.900	6.020	0.004

2.2 Nanocomposites and multilayers

Nanocomposites are considered as they could reduce the dose of incoming radiation reaching the interiors of a spacecraft. The used nanofiller is Nanocyl® NC7000™ consisting of multiwalled carbon nanotubes (MWCNTs) obtained through catalytic chemical vapor deposition (11). Configurations with Reverlink® matrix and CNT concentrations from 0.1% to 1% are studied to look for a trade-off between radiation shielding and self-healing behavior of the material, as the insertion of these fillers usually decreases the healing performance.

Multilayer specimens are investigated to assess the effect of coupling the polymers with another layer on the self-healing performance. The polymer is coupled either with aramid fabric or a 1.6 mm-thick silicone elastomer. In the aramid-Reverlink® case the resin is poured on top of the aramid fibers, while for the remaining configurations the already cured polymers are re-heated and coupled with the elastomer by applying pressure on the layers. For the sake of clarity, the elastomer-Reverlink® multilayer configuration will be here indicated with the ME label.

2.3 Puncture tests

The Reverlink® specimens have a nominal diameter of 60 mm and variable thickness, while the PUU samples have a nominal diameter of 20 mm. In the multilayer case with PUU, 1 mm-thick polymeric layers are used. Examples of specimens are shown in Figure 1.

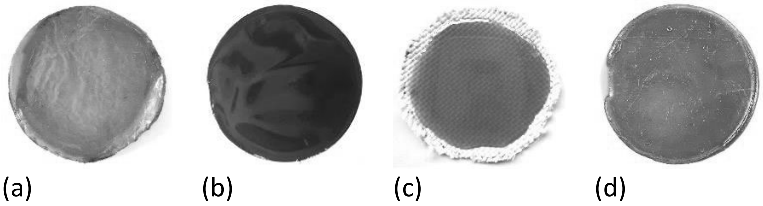
(a) (b) (c) (d)

Figure 1 : Specimens examples - (a) Neat polymer, (b) nanocomposite and (c)(d) multilayers.

After undergoing a 24-hour drying cycle to remove humidity all samples are placed between two polyamide films and mounted on an experimental system for the evaluation of the self-healing performance through acquisition of the resulting leakage flow rate (Figure 2). The samples are fixed on the central cylindrical part of the device and pressurized to 30 kPa relative pressure with continuous air supply to reproduce the conditions inside a space suit, used as a reference. A vertical sinusoidal motion is imposed to the puncheon, setting 9.62 mm amplitude and 0.14 Hz frequency to obtain a velocity of 8.467 mm/s when the puncheon penetrates the specimen, coherently with the ASTM F1342/F1342M-05 standard. Each specimen is tested three times, and maximum and minimum flow rates, the time between them and the air volume lost in a reference time are collected as self-healing performance indicators.

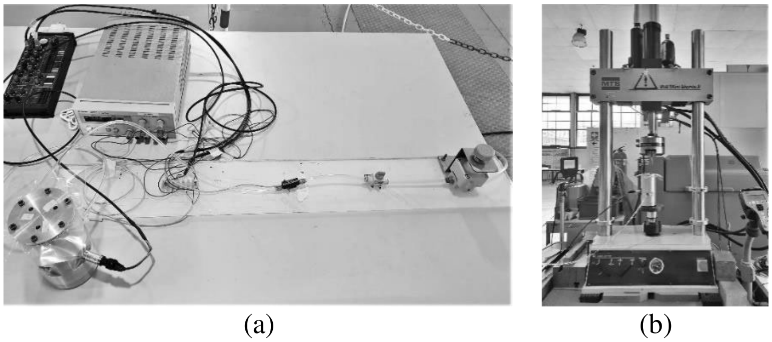
(a) (b)

Figure 2: (a) Testing system; (b) MTS 858 Mini Bionix® II machine for puncture tests.

2.4 Experimental setup for irradiation

The neat PUU samples are exposed to 100 Gy radiation doses emitted at 11.1 Gy/min rate by a Cobalt-60 source placed at a distance of 60.96 cm from the target. The irradiation process is performed in air, and the samples are subsequently stored in a cold room to preserve chemical bonds deterioration generated by exposure to gamma rays.

3. Experimental results and discussion

3.1 Puncture tests on non-irradiated samples

Results obtained for the nanocomposites class containing up to 1% CNTs (Figure 3) show that the self-healing ability is mainly related to the specimen's thickness rather than to the concentration of CNTs. Furthermore, complete healing is not reached, and practical issues were also encountered when trying to increase the amount of nanotubes, making this solution less appealing than the multilayer one. In particular, it is observed that coupling the analyzed polymers with the elastomeric layer increases the self-healing performance, while the aramid fabric does not provide a comparable improvement. This is justified by the elastomer's springback behavior, which accelerates the self-healing process by promoting hole closure in the punctured region (Figure 4, Figure 5). In these terms, the multilayer configuration containing the PUU 90 polymer is characterized by the highest average performance (Table 3). This is in contrast with what is found when considering the neat polymers, as in that case the PUU 100 has a slightly better behavior than PUU 90. This might be due to repeatability issues in the experiments and needs to be further investigated.

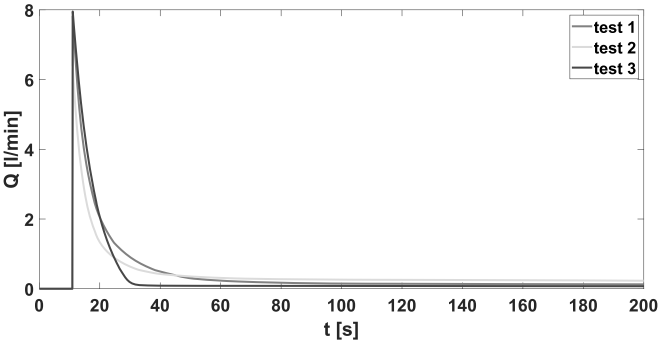

Figure 3: Puncture test results for the CNT nanocomposite.

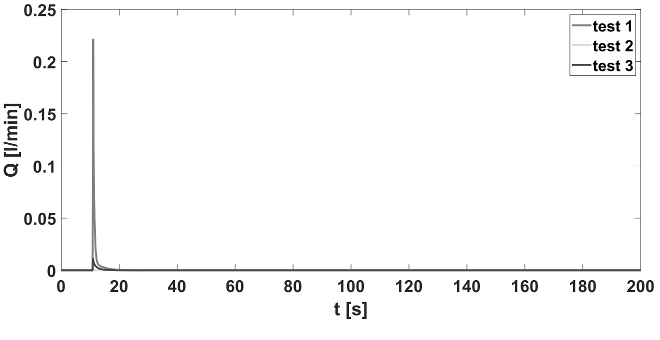

Figure 4: Puncture test results for the ME configuration (Reverlink®-elastomer multilayer).

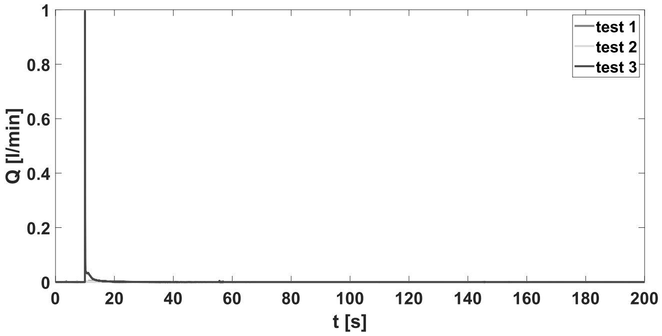

Figure 5: Puncture test results for the PUU 100-elastomer multilayer.

Table 3 : Average results obtained for elastomeric multilayer and nanocomposite specimens.

	Multilayer with elastomer					Nanocomposite
Data	ME	PUU 70	PUU 80	PUU 90	PUU 100	1% CNT
Max. flow rate [l/min]	0.0777	0.4017	0.1860	0.0411	0.3352	7.3830
Min. flow rate [l/min]	0	0	0	0	0	0.1423
Δt to min. flow rate [s]	7.96	99.62	11.44	9.08	10.47	200.00
Leaked volume [l]	0.0005	0.0059	0.0020	0.0004	0.0012	1.2519

The average performance parameters related to ME and PUU 90 multilayers are then compared with results from previous studies (4,12) (Table 4). A space suit bladder with a thickness of 0.289 mm is also considered as a reference. Overall, the best results are related to the PUU 90-elastomer multilayer, but the difference with the ME configuration is small. In both cases, the minimum flow rate is null in all repetitions and the average time to get to it is lower than 10 s, significantly below the healing times of the other materials. The average volume of leaked fluid is two to four orders of magnitude below the other specimens, indicating coupling with a silicone elastomer as a promising solution.

Table 4 : Comparison with results from previous studies (4,12)*.*

Material	Max. flow rate [l/min]	Min. flow rate [l/min]	Time to min. flow rate [s]	Leaked volume [l]
ME average	0.0777	0	7.96	0.0005
PUU 90 multilayer avg.	0.0411	0	9.08	0.0004
Reverlink® + aramid (4)	1.589	0.092	307.13	0.3377
Bladder	2.401	1.032	300.50	3.8968
Sylgard® 30 mil	0.208	0.054	110.00	0.2273
Conathane® 30 mil	1.727	0.249	222.25	0.9960
Rucothane® 15 mil	3.866	1.497	349.70	5.773
TyrLyner® 30 mil	4.523	0.085	153.75	0.524

3.2 Puncture tests on irradiated samples

Comparison of average results related to irradiated and non-irradiated specimens of the same thickness shows that a dose of 100 Gy already significantly deteriorates the healing performance (Table 5, Figure 6). In general, stronger degradation is observed in materials with a higher content of difunctional units. Overall, the best performing polymer is PUU 100, as its strong springback response ensures short healing times and a reduced air leakage after perforation.

Table 5 : Puncture tests results for irradiated and non-irradiated neat PUU 100 samples.

Irradiated	Max. flow rate [l/min]	Min. flow rate [l/min]	Time to min. flow rate [s]	Leaked volume [l]
1	2.8231	0.0281	189.69	0.1453
2	3	0.0171	189.57	0.1003
3	2.6221	0.0503	188.61	0.2861
Non irradiated				
1	1.2549	0	5.66	0.0025
2	1.7352	0.0147	189.80	0.1057
3	1.5489	0	4.84	0.0017

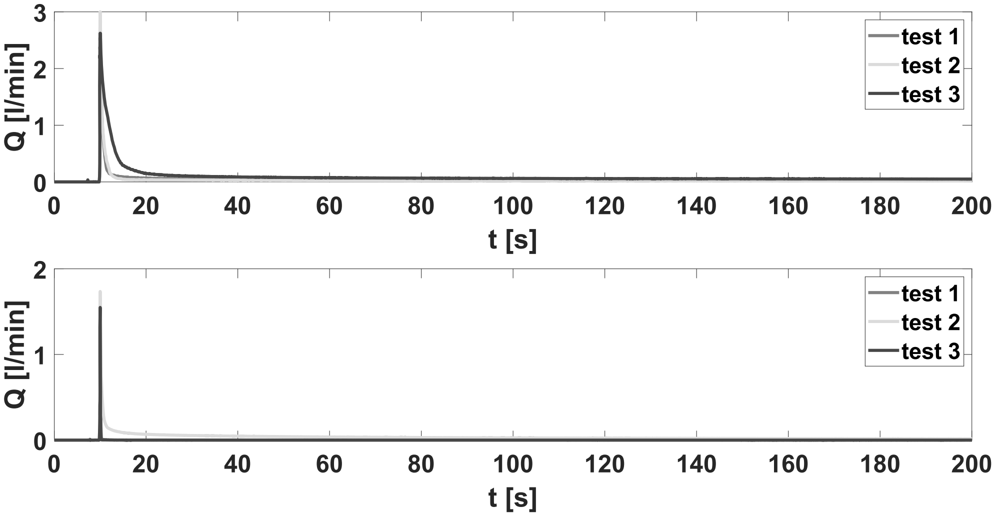

Figure 6: Puncture tests comparison for irradiated and non-irradiated neat PUU 100 samples.

4. Conclusions

4.1 Final considerations

Results obtained through coupling with the elastomeric layer show significant improvements with respect to previous studies. This type of configuration can be optimized through a trade-off between thickness reduction and preservation of the self-healing properties.

Furthermore, polymers containing a higher content of difunctional moieties present a higher viscoelastic response and a better healing efficiency, while specimens with higher cross-linking density are characterized by a larger elastic and subsequent springback response. An optimal healing performance is hence ensured by a good trade-off between elastic and viscous behavior, as the former allows fast contact between the edges of a damaged area, and the latter is necessary for sealing. Overall, the most promising solution is the multilayer configuration coupling the elastomer with PUU 90. In addition, results are highly influenced by local thickness, while humidity is crucial only when considering Reverlink®.

Concerning the effects of space radiation, it can be stated that even a limited dose such as 100 Gy is sufficient to deteriorate the materials' healing performance.

As a general conclusion, a self-healing layer could indeed significantly increase safety, reliability, and lifetime of spacecraft for future missions. However, further studies must be carried out to succeed in implementing this solution.

4.2 Future work

To achieve more accurate and repeatable experimental results, the tests could be performed in a controlled environment, for example by including the test apparatus in a vacuum chamber. As a matter of fact, self-healing polymers are in general sensitive to factors such as temperature and humidity. The variability of the results, which is partially due to the non-uniformity in the samples' thickness, could be limited through more accurate manufacturing techniques.

Specimens could be subjected to higher radiation doses and dose rates to better evaluate how radiation affects self-healing. To prevent material oxidization and analyze the evolution of radicals, irradiation could be performed in an inert environment, such as in liquid nitrogen. In general, further characterization will be performed to assess and better understand the effects of space environment on the self-healing ability of the analyzed materials. In these terms, the samples will also be exposed to UV irradiation, thermal cycling, atomic oxygen.

Acknowledgements

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5. References

1. Rask J, Vercoutere W, Navarro BJ, Krause A. Space faring: the radiation challenge, an interdisciplinary guide on radiation and human space flight. 2008.
2. Ghosh SK, editor. Self-healing materials-Fundamentals, design strategies, and applications. Wiley-VCH; 2009.
3. Pernigoni L, Lafont U, Grande AM. Self-healing materials for space applications: overview of present development and major limitations. CEAS Sp J. 2021;(0123456789).
4. Pernigoni L, Grande AM. Development of a supramolecular polymer based self-healing multilayer system for inflatable structures. Acta Astronaut [Internet]. 2020;177(April):697–706. Available from:

https://doi.org/10.1016/j.actaastro.2020.08.025

5. Grande AM, Martin R, Odriozola I, van der Zwaag S, Garcia SJ. Effect of the polymer structure on the viscoelastic and interfacial healing behaviour of poly(urea-urethane) networks containing aromatic disulphides. Eur Polym J. 2017;97.
6. Rekondo A, Martin R, Ruiz de Luzuriaga A, Cabañero G, Grande HJ, Odriozola I. Catalyst-free room-temperature self-healing elastomers based on aromatic disulfide metathesis. Mater Horiz [Internet]. 2014;1(2):237–40. Available from: http://xlink.rsc.org/?DOI=C3MH00061C
7. Montarnal D, Tournilhac F, Hidalgo M, Leibler L. Epoxy-based networks combining chemical and supramolecular hydrogen-bonding crosslinks. J Polym Sci Part A Polym Chem [Internet]. 2010;48(5):1133–41. Available from: https://onlinelibrary.wiley.com/doi/full/10.1002/pola.23870
8. Sordo F, Mougnier SJ, Loureiro N, Tournilhac F, Michaud V. Design of Self-Healing Supramolecular Rubbers with a Tunable Number of Chemical Cross-Links. Macromolecules. 2015;48(13):4394–402.
9. Sordo F, Michaud V. Processing and damage recovery of intrinsic self-healing glass fiber reinforced composites. Smart Mater Struct [Internet]. 2016 Aug 1;25(8):084012. Available from: https://iopscience.iop.org/article/10.1088/0964-1726/25/8/084012
10. Arkema. Reverlink supramolecular technology. p. 1–8.
11. Nanocyl. NC7000™–Technical Data Sheet. 2021.
12. Fredrickson TH. NASA research announcement final report for space suit survivability enhancement. 1998.