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Exposure of structural epoxy adhesive to combination of tensile stress and γ-radiation

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ABSTRACT

Mass is money! This sentence applies even more in space transportation than in aviation, due to the enormous cost it takes to carry payload in orbit. With the development of high temperature adhesives and the rise of composite materials like CFRP, adhesive bonding has experienced enormous growth in the space sector. Opposing to terrestrial application, the adhesive joint has to withstand unique environmental conditions. Adhesive systems belong to the group of polymers. Thus, the effect of radiation, especially ionizing radiation, has an enormous influence on the structural integrity of adhesive systems. In a space exploration mission e.g. on the lunar surface, the adhesive has to withstand mechanical loads in combination with radiation environment. This paper investigates the combined effect of tensile stress and γ-radiation on the mechanical properties of a 2-component epoxy adhesive. It's a matter of the greatest importance to investigate the possible degradation of the adhesive in combination with irradiation and tensile loading due to increased chain scission of stressed molecules. For structural adhesives, such phenomena are not covered well in the literature.

In the present work, bulk specimens of the investigated adhesive are milled out from a plate and exposed to a^{60}Co source. During the irradiation they were loaded in tensile direction. Afterwards, the specimens were inspected by FTIR spectroscopy and then tested destructively in order to determine the potentially degraded mechanical properties.

The results show that the mechanical properties of the bulk adhesive stay constant for non-irradiated, irradiated non-loaded and irradiated loaded specimen which concludes that the investigated adhesive is not weakened by the combination of γ-radiation (32.4 kGy) and tensile loading.

1. Introduction

A new space race has begun. This is confirmed by the emergence of private companies in the space sector and the new efforts made by established agencies to advance the exploration of the moon and so on [1]. Since one of the key requirements of a spacecraft is a high stiffness to weight ratio [2], carbon fiber reinforced plastics (CFRP) are nowadays common in spacecraft design. Furthermore, CFRP structures whether monolithic or as sandwich panels rely on proper adhesive joints [3]. In general, two phases of a space mission are relevant for the structural design of a spacecraft. During the launch phase, enormous loads appear, such as static loads due to acceleration, vibration loads induced by the engines and acoustic loads induced by sound interactions with the structure. In the orbit phase, space represents very harsh environmental conditions like radiation, thermal cycling, atomic oxygen and vacuum which can induce environmental stress and degradation of material properties.

Radiation in space is classified in ionizing and non-ionizing radiation. The first group includes α-,β- and γ-radiation, heavy ions, X-rays as well as higher UV-radiation. Possible sources are the sun, trapped electrons in the earth magnetic field or cosmic particles. The second group includes lower UV-radiation, infrared-radiation and light in the optical wavelength which are also emitted by the sun. In the following the effect of γ-radiation is investigated as it has become a standard in radiation testing for space graded hardware and materials [4,5]. Ionizing radiation influences the mechanical behavior of polymers like adhesives due to effects such as scission of the molecular chains, crosslinking of molecular chains and producing free radicals. Chain scission describes the effect of cutting macromolecular chains in the polymeric bond resulting in a softening of the material. Conversely crosslinking describes the formation of new intermolecular links like covalent bonds. This results in an increase in stiffness as well as brittleness. More

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detailed explanations are given in Refs. [6–8].

Adhesives have to withstand those irradiation effects in their operating time in orbit. However, notable mechanical loads usually don't occur in this phase. Considering an exploration mission e.g. on the Moon or Mars, irradiation and mechanical stresses appear simultaneously: e.g. stress due to weight or atmospheric pressure in a habitat. Thus, the combined effect of radiation and tensile stress on the 2-component structural epoxy 3 M SW9323 is investigated.

There is an amount of works which investigated the effect of irradiation in combination with mechanical stress on polymers. Some researchers focused on thermoplastics like poly(methyl methacrylate) (PPMA), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene (PE) [9–12]. Others deal with pure epoxy resins, chemically similar materials [13,14] or composites that use epoxy matrix [15–18]. Bell et al. investigated the creep behavior of PMMA, PVC and PS under a radiation dose of 1.5 MGy [9]. This study showed that radiation induced creep starts immediately after exposure to the radiation source. For some materials this effect continues after the radiation, e.g.: PPMA. Wang et al. showed that γ-radiation induces cross-linking in ultra-high molecular weight polyethylene [10]. Using a dose of 300 kGy the creep resistance, Young's modulus and the operational temperature increased. Stepanov used electron beams to investigate the behavior of PC and PS under a load controlled creep test in combination with irradiation [12]. Both polymers showed an irreversible increase in strain regardless of the radiation dose. The authors claimed that this effect can be ascribed to some active substances that occurs in the stressed polymers and change their structure. Hill et al. investigated the effect of combined tensile stress and electron beam radiation on bisphenol-A polysulfone [14]. They proposed the mechanism of enhanced chain scission of stressed bonds but only show that the rate of creep during radiation is increased.

Nishiura et al. investigated the mechanism of irradiation-induced creep on pure epoxy resin [13] and epoxy based composites [17,18]. Three-point bending tests were conducted under electron beam radiation with a total dose of 8 MGy in a liquid nitrogen environment of 77 K. The result showed that the creep during radiation was much higher than the creep of specimen tested after radiation. Nishiura proposed radiation-induced molecular chain scission was the mechanism leading to this. Additionally, electron spin resonance analysis suggests that the Young's modulus decreases for specimen subjected to simultaneous irradiation and mechanical load.

Rojdev et al. investigated the combined effect of radiation and mechanical load on composite materials with epoxy matrix [16]. Their motivation was a simulated long-term lunar expedition including a habitat with a skin stiffened laminate as a pressure vessel shell. Due to the radiation environment on the lunar surface, a combination of irradiation and biaxial loading on the pressure vessel were simulated. Two different dose rates were used. For 1.5 Gy/s the predominance of crosslinking in the matrix material (epoxy) was proposed whereas for 0.14 Gy/s chain scission in the matrix seemed to be predominant. Most of the mentioned works showed a decrease in creep behavior as well as other mechanical properties like bending stiffness, whereas Suwanprateeb et al. found an increase in creep resistance of polyethylene composites that were exposed to γ-radiation up to a dose of 25 kGy [19].

None of the discussed literature investigates the change of mechanical properties like Young's modulus, shear modulus and tensile strength after simultaneously exposure to radiation and mechanical stress for a structural adhesive. Furthermore, a spectral analysis of such an adhesive after this combination of environment has not been carried out yet.

2. Experiments

In the current work, bulk specimen of the structural epoxy adhesive 3 M SW9323 (without fillers) were exposed to a combination of radiation environment and tensile loading. Thus, a tensile loading fixture was designed. Specimens were milled out from plates, inserted in the fixture and exposed to the radiation. Afterwards, the chemical composition of the specimens was investigated using Fourier-transform infrared (FTIR) spectroscopy and the mechanical properties of the specimens were determined by using an electronic tensile loading machine and digital image correlation (DIC) technique.

2.1. Specimen manufacturing

The specimen manufacturing process is as following: The 2-component epoxy adhesive is first mixed with a ratio of 100:27 manually. To reduce the trapped air inside the mixture, a vacuum mixer was used. After this, the mixture was poured into a PTFE mould. The design of this mould is covered in Ref. [6]. The curing process inside the mould took place at room temperature for 24 h. The result of this process is a plate of 3 M SW9323 with the dimensions of 290 mm × 190 mm. This plate is cured for additional 14 days at room temperature regarding the technical datasheet [20]. Afterwards, the specimens were milled out of the plate using a CNC milling center. The specimens geometry is based on ASTM D412 [21].

Altogether 5 different specimen sets, each representing a different environmental configuration were manufactured (see Table 1). Each set consists of five specimens. The unirradiated were chosen as the reference set. Set 2 and set 3 were irradiated but not loaded during irradiation. To investigate potential interactions with the atmosphere, mainly with the oxygen during radiation, set 3 was vacuum sealed during irradiation. Set 4 and 5 were tensile loaded with different load levels. Namely 11.52 MPa for Set 4 and 20.78 MPa for Set 5. The tensile strength of non-irradiated 3 M SW 9323 is $\sigma_{max} = 42$ MPa.

2.2. Radiation environment

The ^{60}Co source at Helmholtz-Zentrum Berlin was used to provide the radiation environment for the current work. The source emits β- and γ-radiation although the electrons (β-particles) are absorbed in a stainless steel shielding (see Fig. 2) to provide a pure γ-radiation environment. The specimens were irradiated for nine days under a dose rate of 2.5 Gy/min which added up to a total dose of 32.4 kGy. Dose rates were measured by PTW Unidos universal dosimeter with a Farmer ionization chamber type 30012.

2.3. Tensile loading fixture

In order to achieve tensile loading in this radiation environment, a fixture was designed, that fulfills the following requirements: The most inner diameter has to be larger than the 120 mm outer diameter of the ^{60}Co source to fit around. The specimen's radial distance to the source is minimized to increase the dose rate and save irradiation time. Due to a large variability of the source's dose rate in z-direction, the specimens were positioned around 120 mm above ground. At this height the gradient is at its minimum. Tensile loading is introduced by Z-223HX metal extension springs by Gutekunst Federn. Fig. 3 shows its load-displacement curve. Springs as loading devices offer the advantage of a linear load-displacement behavior over a large range of displacement. Potential creep of the specimen will not result in a significant load drop. In addition, the amount of tensile loading can be adjusted accurately.

Table 1
Specimen overview.

Set	Load [N]	Displacement [mm]	Stress [MPa]	σ/σ_{max}	
1	0	0	0	–	non-irradiated
2	0	0	0	–	irradiated
3	0	0	0	–	irradiated in vacuum
4	368.6	15	11.52	0.27	irradiated
5	665.1	30	20.78	0.49	irradiated

The total design of the fixture should be robust, which means that no electronic or radiation sensitive parts are obstructed. The fixture provides space for 10 specimens and is made of aluminum, see Fig. 4. The weight including the specimens is 42 kg. In the following the installation procedure of a specimen in the fixture is given:

- Bolt down the specimen to the upper and lower clamp. This should be done on a flat surface in order to prevent misalignment
- Bolt the assembly to the lower baseplate and support the upper clamp in order to minimize any stress of the specimen
- Screw one eyebolt to the upper clamp
- Screw one eyebolt in the upper baseplate
- Install the spring between both eyebolts
- Start tightening the loading nut until the required load is reached

2.4. FTIR spectroscopy

FTIR was used to investigate the chemical modifications of the adhesive after irradiation. Each specimen was analysed using a Nicolet iS 10 spectrometer by Thermo scientific. The specimen was clamped down to the spectrometer by tightening screw. The location in which the FTIR analysis was carried out is exactly in the middle of the specimen, marked in Fig. 1. The ambient atmosphere was recorded in order to avoid measuring errors that could be caused by molecules in the air. The transmission spectra of the irradiated specimens is compared with non-irradiated ones (Fig. 7).

2.5. Tensile test

Using the electro universal testing machine Instron 5567, mechanical properties of the specimen are determined. The procedure is based on ASTM D638-14 [22] with a displacement controlled rate of 2 mm/min. Strain is measured using DIC technique (GOM Aramis 4 M). Detailed information regarding the setup can be found in [6]. The data acquisition frequency is 2 Hz. The DIC controller records the analog signal of the Instron's load cell to correlate with the optical measured strains. All tests are carried out until complete failure of each specimen. Fig. 5 shows the setup of the tensile test, including testing machine, clamping jaws, DIC cameras and lights. On the left, the Aramis 4 M system is shown. On the right a detailed picture of a specimen with stochastic pattern is pictured.

3. Results and discussion

After exposing the bulk specimen of 3 M SW9323 to a combination of radiation and tensile stress, the tensile loading fixture was disassembled. A clear discoloration can be seen with the naked eye (Fig. 6). All irradiated specimens, namely set 2–5 seem to undergo the exact same discoloration, an effect that was observed in the previous study [6].

To investigate a molecular change induced by the combination of irradiation and tensile stress, the specimen were examined via FTIR spectroscopy. Fig. 7 shows the transmission spectra for all 5 specimen sets. Each spectra represents the mean values of all 5 specimen spectra for each set. The spectra around characteristic chemical groups which are often contained in epoxy adhesives are magnified. It shows that Set 3 (irradiated under vacuum) in general has the highest transmission compared to the other sets. For the C–H group, set 1 has the lowest transmission value followed by set 2. For the C═C and C–O groups set, 1 has the smallest value, whereas for the C═O group it has the highest

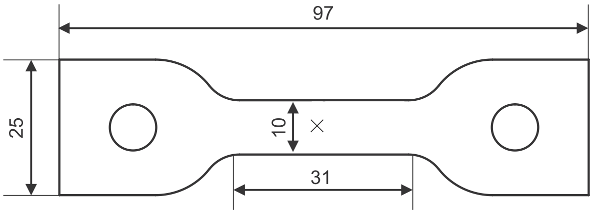


Fig. 1. Bulk specimen, X marks the location of FTIR measurement (dimensions in mm).

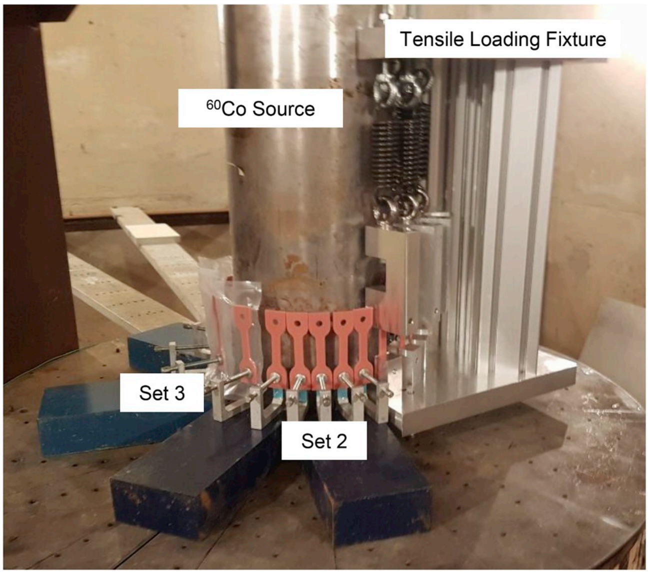


Fig. 2. Radiation facility at helmholz zentrum Berlin.

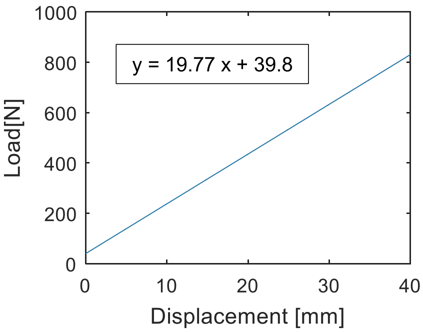


Fig. 3. Load displacement curve of the Z-223HX spring.

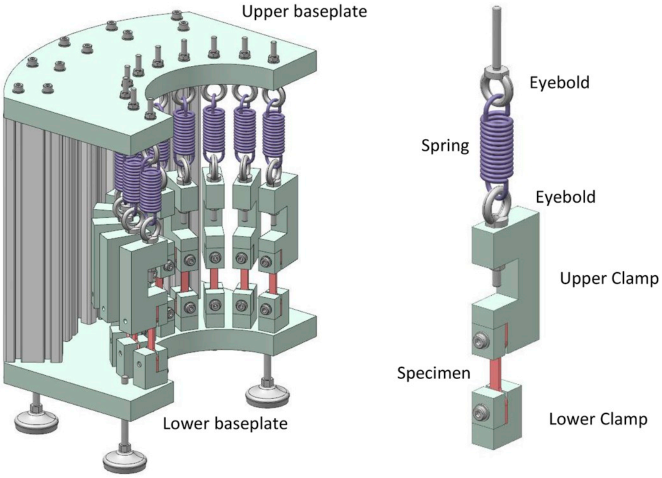


Fig. 4. Tensile loading fixture.

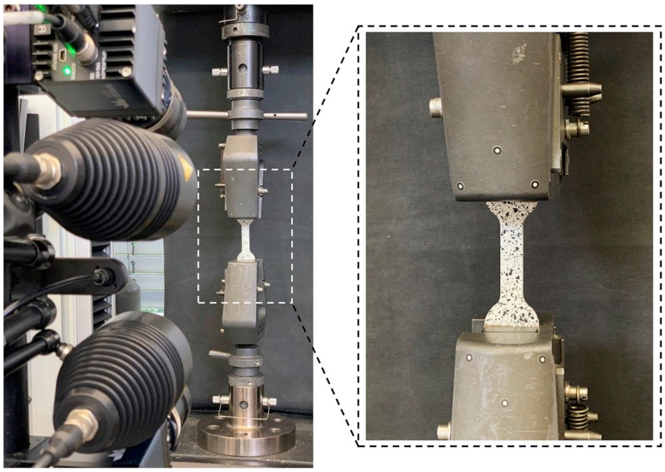


Fig. 5. Setup for tensile test including DIC system (left) and detailed view of the specimen (right).

Fig. 6. Irradiated specimen after tensile test (left) and non-irradiated specimen (right).

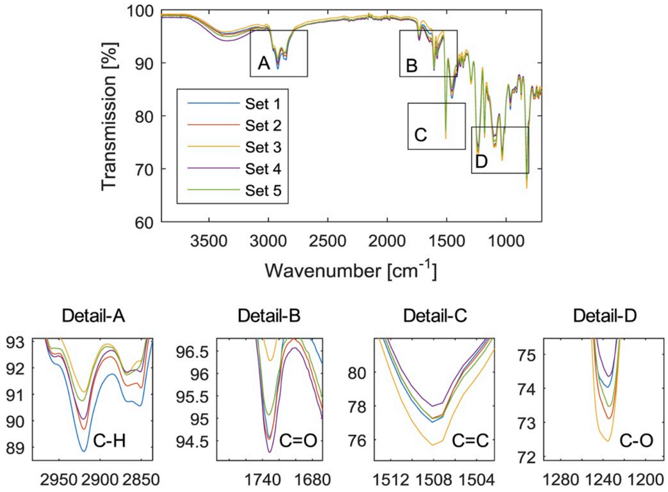


Fig. 7. FTIR Spectrum of the Specimen Sets after irradiation.

value. A low transmission value corresponds to high interaction of the infrared photons with a certain characteristic group in the specimen leading to the assumption that an increase in transmission corresponds to reduction of those groups. According to Djouani et al. [23] this is an indication of chain scission.

Altogether a clear trend is not observable. For some characteristic groups, the irradiated and tensile loaded specimen sets have the highest transmission value. For other groups this is not the case and the non-irradiated set has the highest value. This might be explained by the claim that the radiation induced crosslinking and chain scission effects level each one out.

After FTIR analysis, the specimens were tested under tensile loading. Young's modulus, shear modulus and tensile strength were determined using the load signal from the electro universal testing machine Instron 5567 and the strain measured by DIC technique. Stress-strain-curves for all tested specimens are shown in Fig. 8, each set separately. All curves possess a similar slope and reach a maximum stress of around 42 MPa. After the maximum stress is reached, a distinct plastification zone is observed before the specimen fails. Crocombe and Adams found a similar trend for bulk epoxy adhesive [24]. Some specimens, e.g. 6, 14 and 15 failed at a smaller strain. The reason are defects inside the specimen, induced by the mixing process. Comparing those defects to the ones in previous investigations [6], the size and number is drastically reduced due to vacuum mixing. Young's modulus E (equation (2)), shear modulus G (equation (3)) and tensile strength σ_{max} (equation (1)) are determined as following

$$\sigma_{yy} = \frac{P}{A} \tag{1}$$

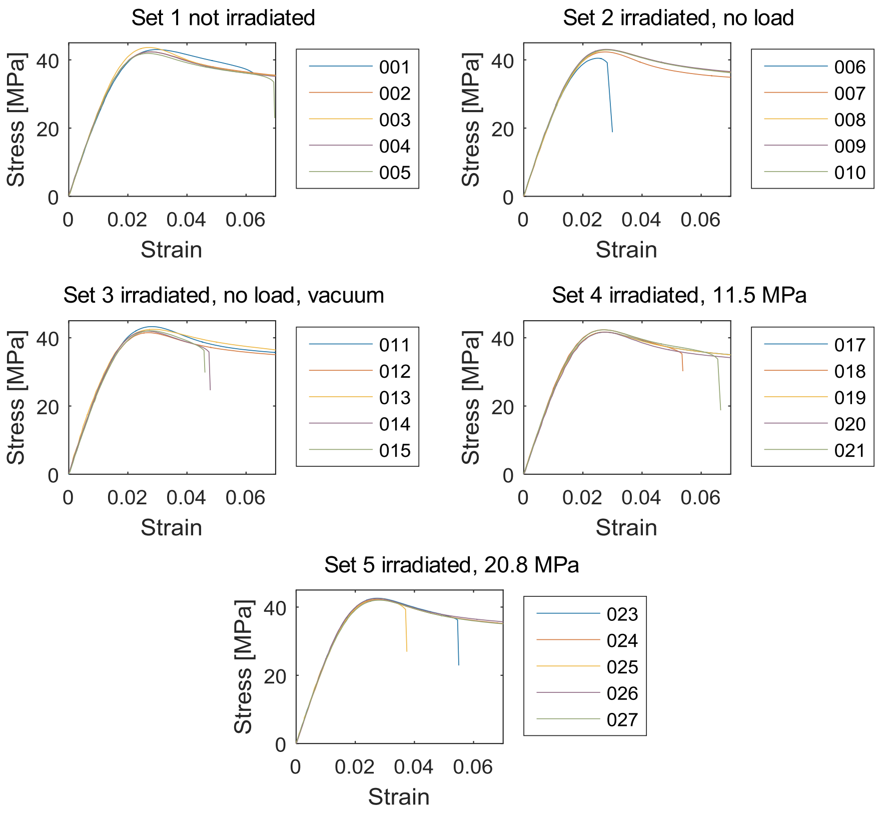
$$E = \frac{\sigma_{yy}}{\varepsilon_{yy}} \tag{2}$$

$$G = \frac{E}{2(1+\nu)} = \frac{\sigma_{yy}}{2(\varepsilon_{xx} - \varepsilon_{yy})} \tag{3}$$

where σ_{yy} is the stress in axial direction, P is the load of the testing machine, A is the area of cross section of the specimen before the test. ε_{yy} is the strain in axial direction and ε_{xx} the strain in lateral direction. Table 2 shows the mean values for the determined mechanical properties of each specimen group. In addition, the standard deviation is given. It shows that Young's modulus is almost in the same range for all sets. Varying from 2330 ± 47 MPa for set 1 to 2357 ± 51 MPa for set 5. The same trend can be observed for the shear modulus and the tensile strength respectively. The difference of the mean values of each set stay in the range of standard deviation. This concludes that the irradiation or the combination of tensile stress and irradiation has no effect on the mechanical properties of 3 M SW9323 bulk specimen, at least in the dose range up to 32.4 kGy. This might be explained by the FTIR spectra. Chain scission and crosslinking occur simultaneously and level each other out, so that the macroscopic mechanical behavior of the adhesive stays unchanged. However there is no concrete evidence for this. Another possible explanation is that the radiation dose is too small to change the mechanical properties of the adhesive. Potential influence of the atmosphere during irradiation, in terms of creating oxygen radicals can also be excluded. The properties of set 3, which were vacuum sealed during irradiation stay in the same range as set 1 (non-irradiated) and set 2 (irradiated) under normal atmosphere.

4. Conclusion

In this study, the combined effect of tensile loading and γ-irradiation on the mechanical properties of a 2-component structural epoxy adhesive 3 M SW9323 has been investigated. For this, bulk specimens of the adhesive were produced. After vacuum mixing, the adhesive was casted into plates using a PTFE mould. The designated specimen shape was milled. 5 different specimen sets with 5 specimens each were produced.


Set 1 not irradiated

Set 2 irradiated, no load

Set 3 irradiated, no load, vacuum

Set 4 irradiated, 11.5 MPa

Set 5 irradiated, 20.8 MPa

Fig. 8. Stress-strain-curves of the tensile tests for all specimen sets.

Table 2

Mechanical properties of the tested specimen sets.

Set	Young's Modulus [MPa]	Shear Modulus [MPa]	σ_{max} [MPa]
1	2330 ± 47	823 ± 31	42.6 ± 0.6
2	2323 ± 40	799 ± 40	42.3 ± 1.0
3	2406 ± 160	806 ± 85	42.3 ± 0.6
4	2343 ± 49	804 ± 59	41.9 ± 0.3
5	2357 ± 51	829 ± 21	42.3 ± 0.2

A unique designed tensile loading fixture was used to put the specimens under tensile load during irradiation using a^{60}Co source. As a reference, one set of specimens stayed non-irradiated and two others were not loaded during irradiation. One of these two sets was vacuum sealed to investigate a potential influence of the atmosphere. After irradiation, the specimen's chemical composition was investigated using FTIR spectroscopy prior to tensile tests to determine mechanical properties. The results show no difference between non-irradiated, irradiated-unloaded and irradiated-loaded specimens. Neither in the transmission spectra or in the stress-strain curve. The standard deviation of the mechanical properties like Young's modulus, shear modulus and tensile strength is small for all specimen sets, namely 2–6%.

This concludes to the claim that γ-radiation up to a dose of 32.4 kGy in combination with tensile loading do not weaken the bulk properties of the investigated epoxy adhesive 3 M SW3923. To proof the radiation resistance of 9 M SW 9323 in future works, the influence of irradiation on the adhesion properties of a joint should be investigated. So far only the cohesion properties have been investigated.

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