2024 International Topical Meeting on Nuclear Applications of Accelerators

EFFECT OF RADIATION ON NATURAL RUBBER AND SILICONE RUBBER COMMONLY USED IN MEDICAL DEVICES AND APPLICATIONS

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Outline

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  - Swelling Ratio, Gel Content and Crosslink Density Calculations
- Conclusions

Project Objectives

Investigate radiation effects on natural rubber and silicone rubber by comparing gamma and e-beam irradiations

Analyze the change in the mechanical, thermal, structural and morphological characteristics of the non-irradiated and irradiated polymers used in medical applications

Compare gamma and e-beam irradiations to determine the degradation and modification pathways

Radiation Sterilization of Medical Devices

Sterilization is defined as the process by which all-living cells, viable pores, viri and viriods are either destroyed or removed from an object.

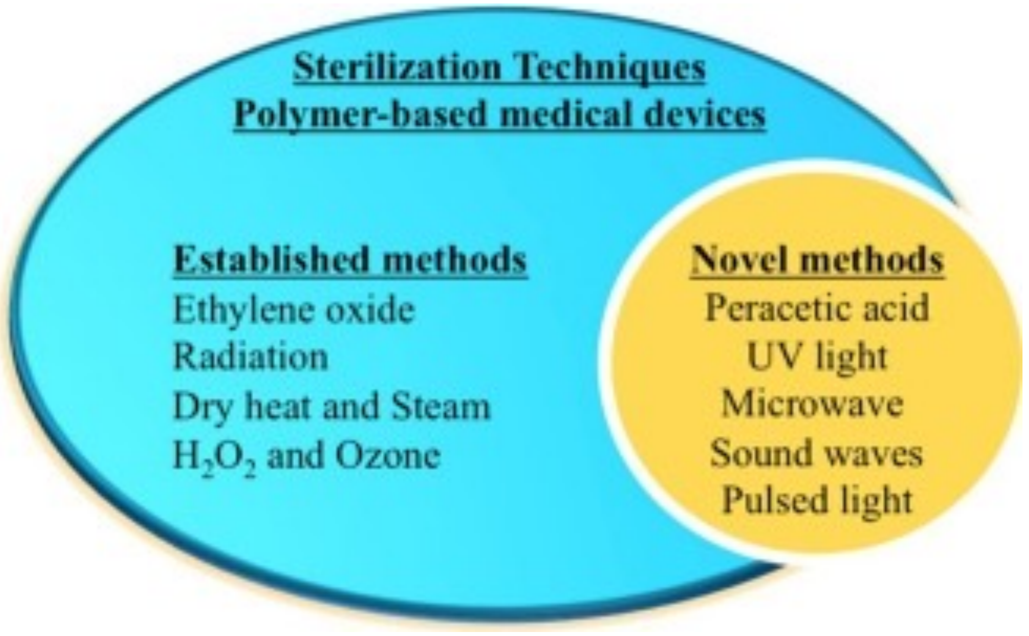


Fig.1*. Sterilization Methods for polymer-based medical devices

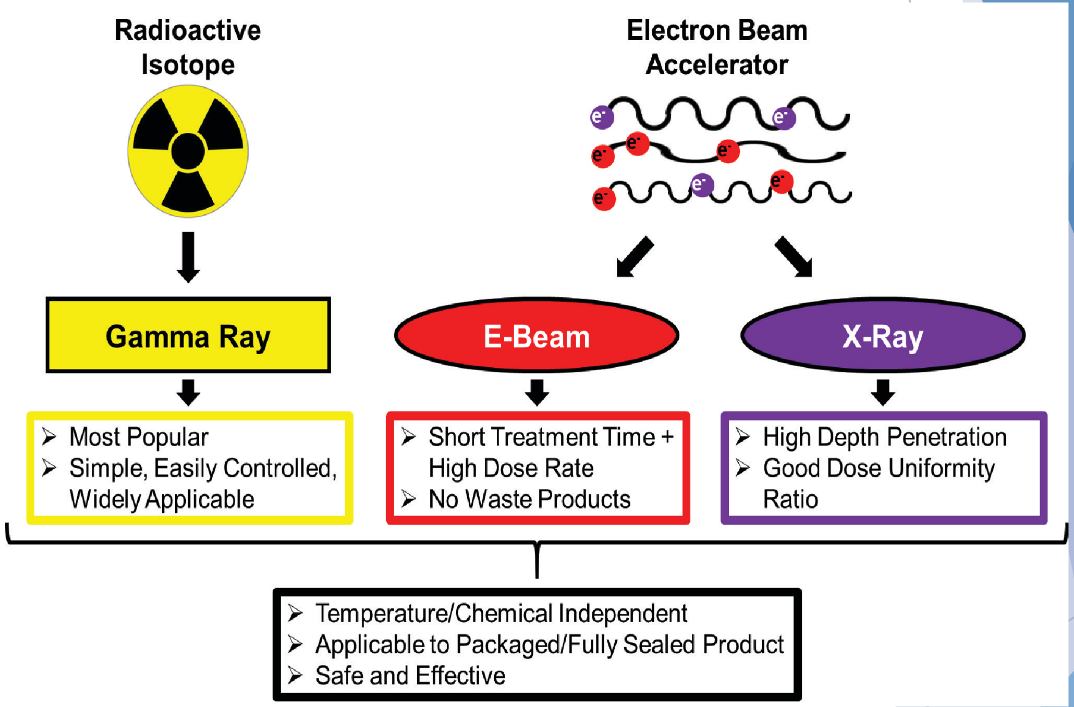


Fig.2.** Comparison of radiation sources for radiation sterilization

* Int. J. Pharm,455-460.doi: 10.1016/j.ijpharm.2017.12.003, 2017. "Sterilization of implantable polymer-based medical devices: A review"
** B. P. Fairand, Radiation Sterilization for Health Care Products: X-Ray, Gamma, and Electron Beam (CRC Press, 2001).

Radiation Effects on Polymers

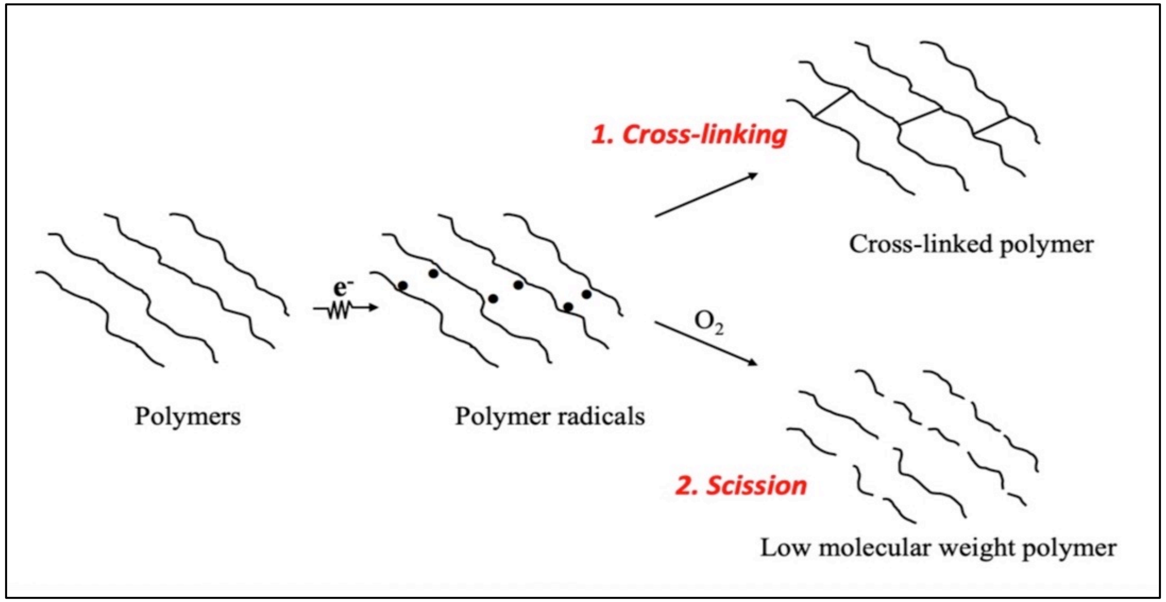


Fig 3. Effect of radiation on polymer chains

The radiation-induced changes depends on:

- Type of the polymer,
- Additives used to compound the polymer,
- Processing of the polymers,
- Irradiation conditions (absorbed dose, dose rate and irradiation atmosphere)

The major chemical changes by ionizing radiation:

- Cross-linking and scission of the polymeric chains,
- Formation of gases, LMW radiolysis products, unsaturated bonds,
- Oxidation of the polymer,
- post-irradiation "ageing”

Materials

Natural Rubber (NR) and Its Medical Applications

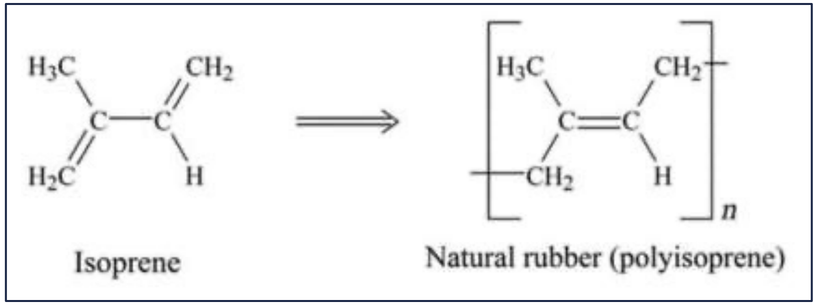


Fig.4. The molecular structure of natural rubber

Medical Applications of NR

- Membranes
- Diaphragms
- Urinary Catheters
- Gaskets, caps, tubes
- Gloves, ballons,pacifiers

Silicone Rubber (SR) and Its Medical Applications

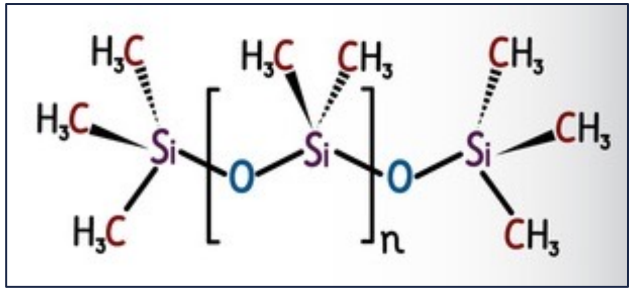


Fig.5. The molecular structure of silicone rubber

Medical Applications of SR

- Catheter and drainge tubing
- Respiratory Care Products
- Ear plugs and hearing aids
- Gasketing material
- Drug Delivery Systems
- Seals, stoppers, valves and clips

Determination of the Vulcanization Parameters for NR and SR

Medical Grade NR (SVR-3L)

Sulfur Vulcanization

Materials	Amounts (phr)
Natural Rubber	100
ZnO	3
Stearic Acid	1
TMDT	2
ZDBC	1.2
Sulfur	1.5

Moving Die Rheometer

Vulcanization Parameters

160ºC / 10 min

150ºC / 10 min

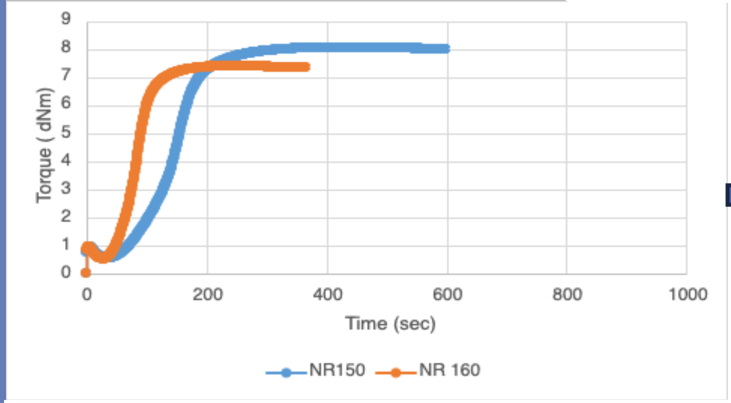


Fig.6. Curing profiles of NR at different temperatures

160ºC / 9 min

Medical Grade SR (Midgold)

Platinum Catalyst Curing

Materials	Amounts (phr)
Silicone Rubber	100
PTC-A (catalyst)	4
PTC-B (cross-linker)	2

Moving Die Rheometer

140ºC - 15 min 2B/1A

150ºC - 15 min 2B/1A

180ºC - 15 min 4B/2A

190ºC - 15 min 4B/2A

180ºC / 15 min

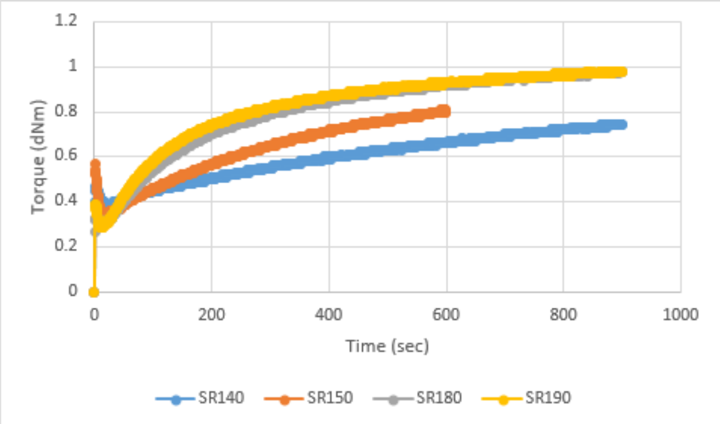
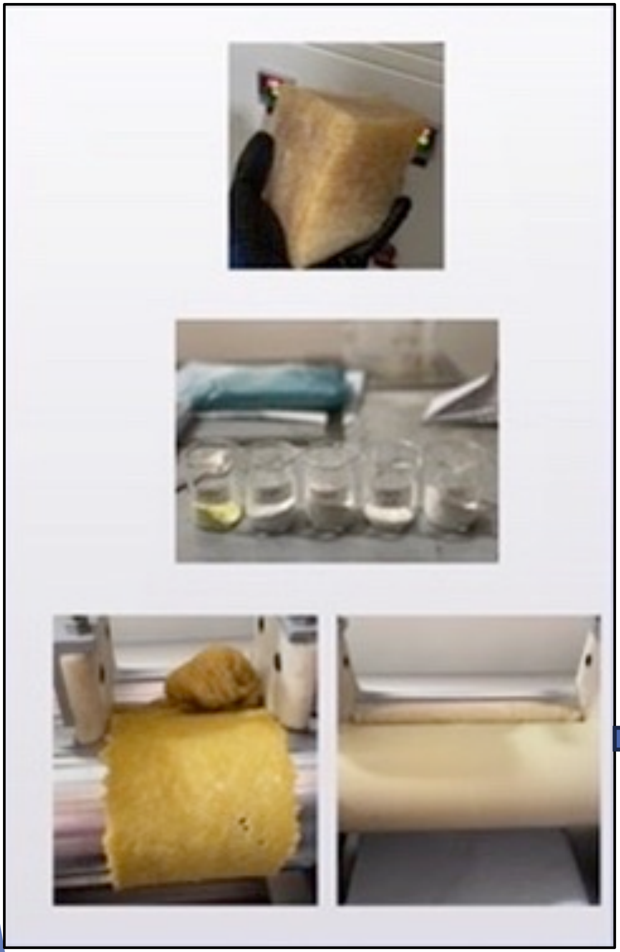
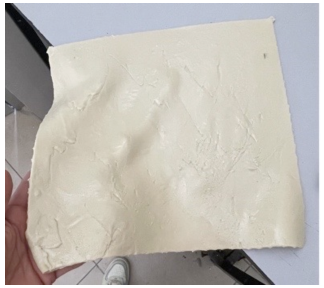


Fig.7. Curing profiles of SR at different temperatures

Manufacturing Process of NR Test Samples



Mastification and compounding of NR



Thermal Hydraulic Press

160°C / 9 min

ASTM D412
ASTM D624

Two-roll mill

NR Test Samples

Fig.8. Preparation of Test Samples from Natural Rubber Compound

Manufacturing Process of SR Test Samples

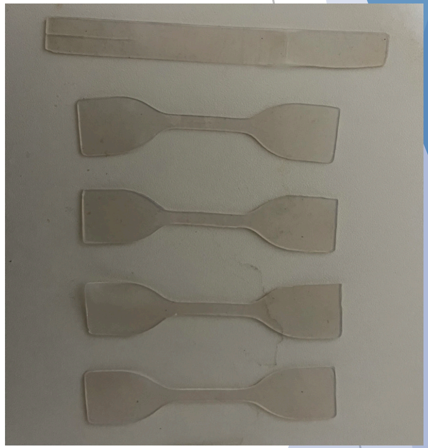
SR compounding process

Thermal Hydraulic Press

180°C / 15 min

Die Cutter

ASTM D412
ASTM D624



SR Test Samples

Fig.9. Curing of silicone rubber and preparation of test specimens

Methodology (Gamma and E-beam Irradiations)

Natural Rubber & Silicone Rubber

Gamma Irradiation

^{60}Co Source – Izotop Observo Sanguis 60 Gamma Irradiator (Turkish Atomic Energy Agency)

H$\dot{D}$: 213 Gy/h
D: 10 kGy
20 kGy
40 kGy
60 kGy
80 kGy

L$\dot{D}$: 19 Gy/h
D: 10 kGy
20 kGy
30 kGy
40 kGy

Fig.10. Izotop Observo Sanguis 60 Gamma Irradiator

E-beam Irradiation

E-beam Accelarator - VIVIRAD - ICT (type 500 keV 20 mA) (Turkish Atomic Energy Agency)

$\dot{D}$: 1kGy/sec

D: 10 kGy
20 kGy
30 kGy
40 kGy
60 kGy
80 kGy
120 kGy

Fig.11. VIVIRAD - ICT type 500 keV 20 mA

Test & Methods

Mechanical Tests

- Universal Testing Machine Schimadzu-AGS X
- 10 kN load cell
- Crosshead speed 50 mm/min
- Average of 3 samples

FTIR Analysis

- Perkin Elmer Spectrum 400
- Resolution: 4 cm^{-1}
- Scans:16
- Range: 4000-400 cm^{-1}
- 6 samples for each irrad.

TGA Analysis

- Perkin Elmer STA 6000
- T: 30-700^{o}C
- Heating rate:10^{o}C/min
- 7 samples for each irrad.

DSC Analysis

- Thermosystem DSC 250,T
- T: -90^{o}C- 0^{o}C
- Heating rate:10^{o}C/min
- 6 samples for each irrad.

SEM Analysis

- Quanta-400F Model
- Various magnific.
- 3 nm Au-Pd coated

Swelling Ratio

- Equilibrium solvent - swelling measurements in toluene.

$$\text{Swelling Ratio (\%)} = \frac{W_f - W_i}{W_i} * 100$$

- 6 sets for each irrad.
- ASTM D471

Gel Content

- Soxhlet Extraction Method

$$\text{Gel Content (\%)} = \frac{wf}{wi} . 100$$

- 6 sets for each irrad.

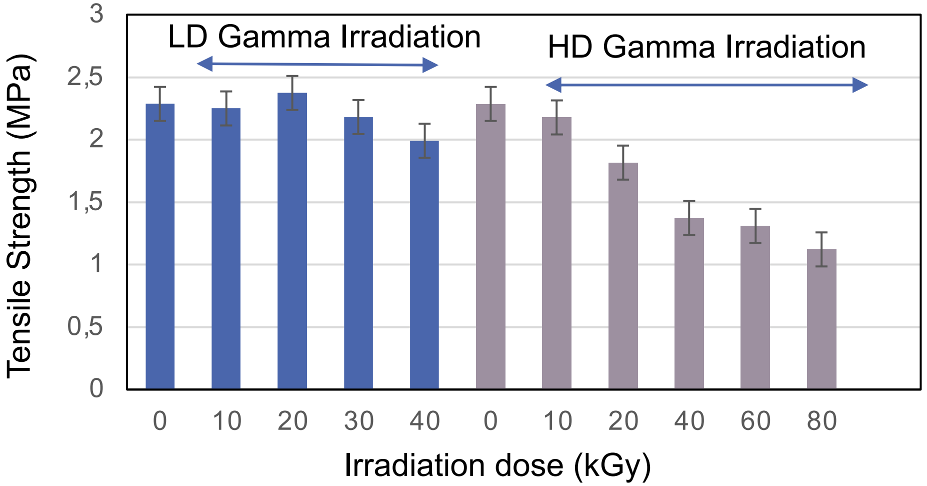
Crosslink Density

- Flory-Rehner Eqn. used

$$\nu = \frac{-\left[\ln(1-V_r) + V_r + xV_r^2\right]}{V_s\left(V_r^{\frac{1}{3}} - V_r/2\right)}$$

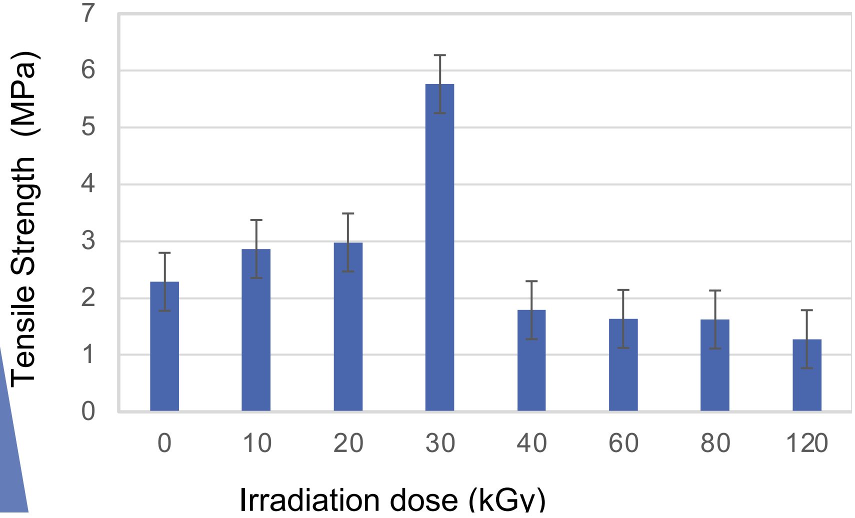
Results (Mechanical Tests for NR)

Gamma Irradiated NR



D⬆ TS⬇

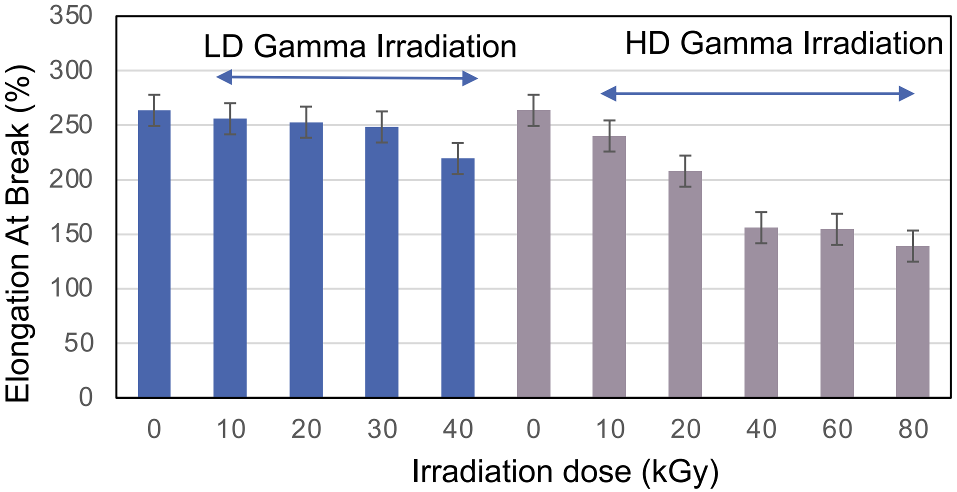
E-beam Irradiated NR



D⬆ TS⬇

Fig.12. Tensile strength values of gamma and e-beam irradiated NR samples at different doses

Gamma Irradiated NR



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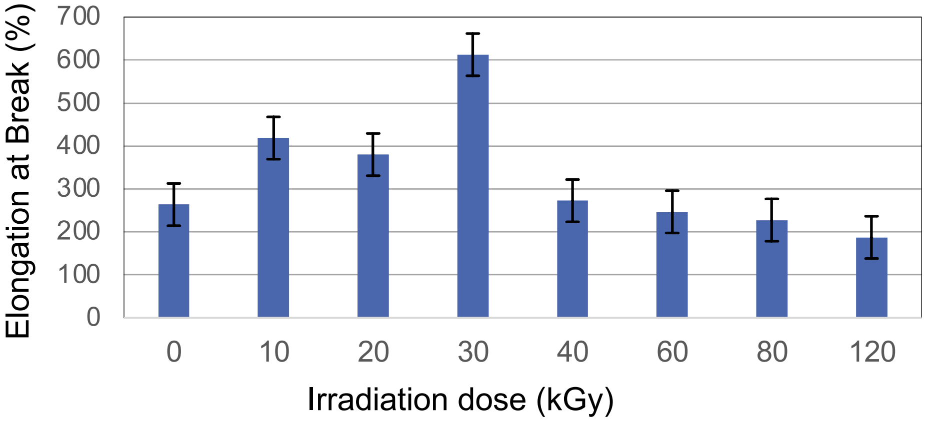
E-beam Irradiated NR



D⬆ EB⬇

Fig.13. Elongation at break values of gamma and e-beam irradiated NR samples at different doses

Results (Mechanical Tests for SR)

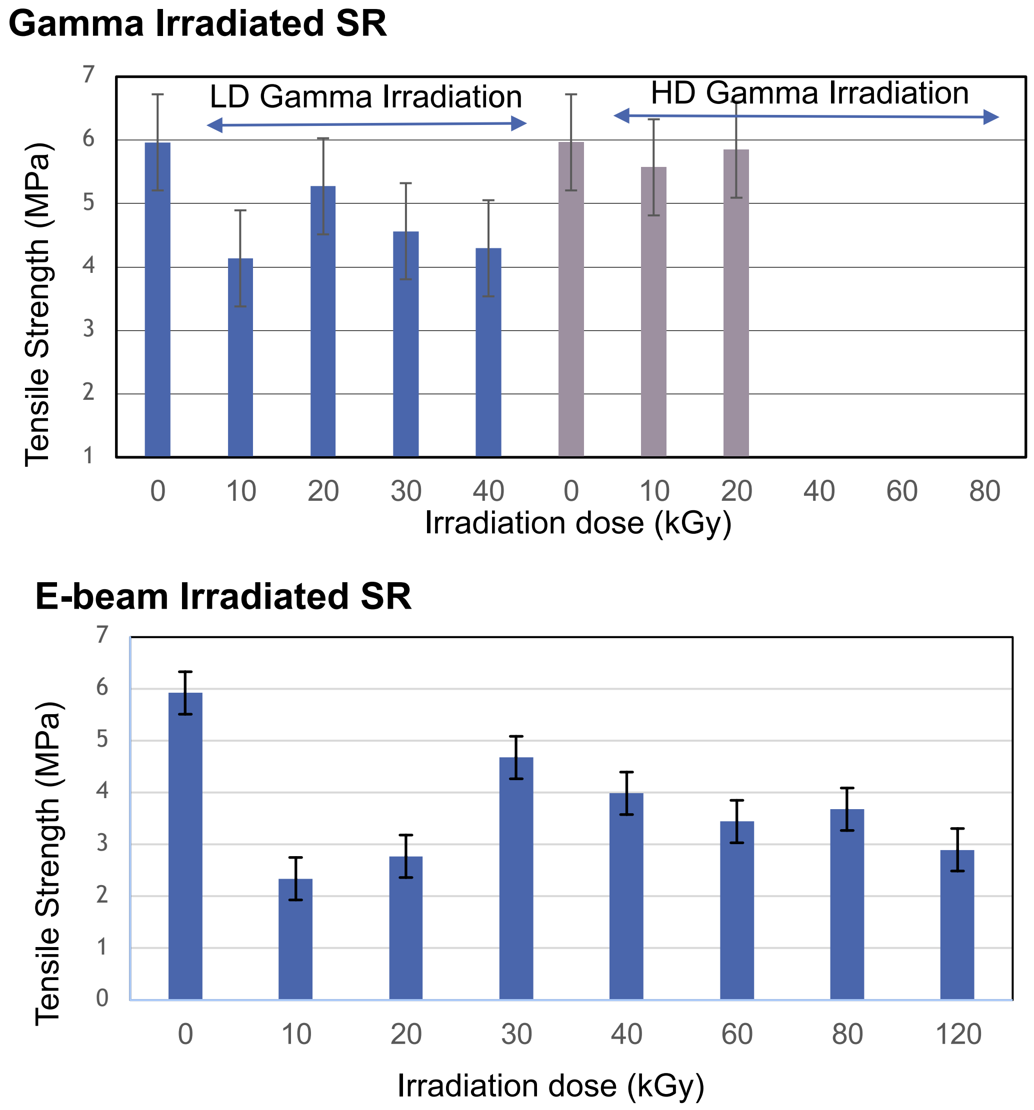


Fig.14. Tensile strength values of gamma and e-beam irradiated SR samples at different doses

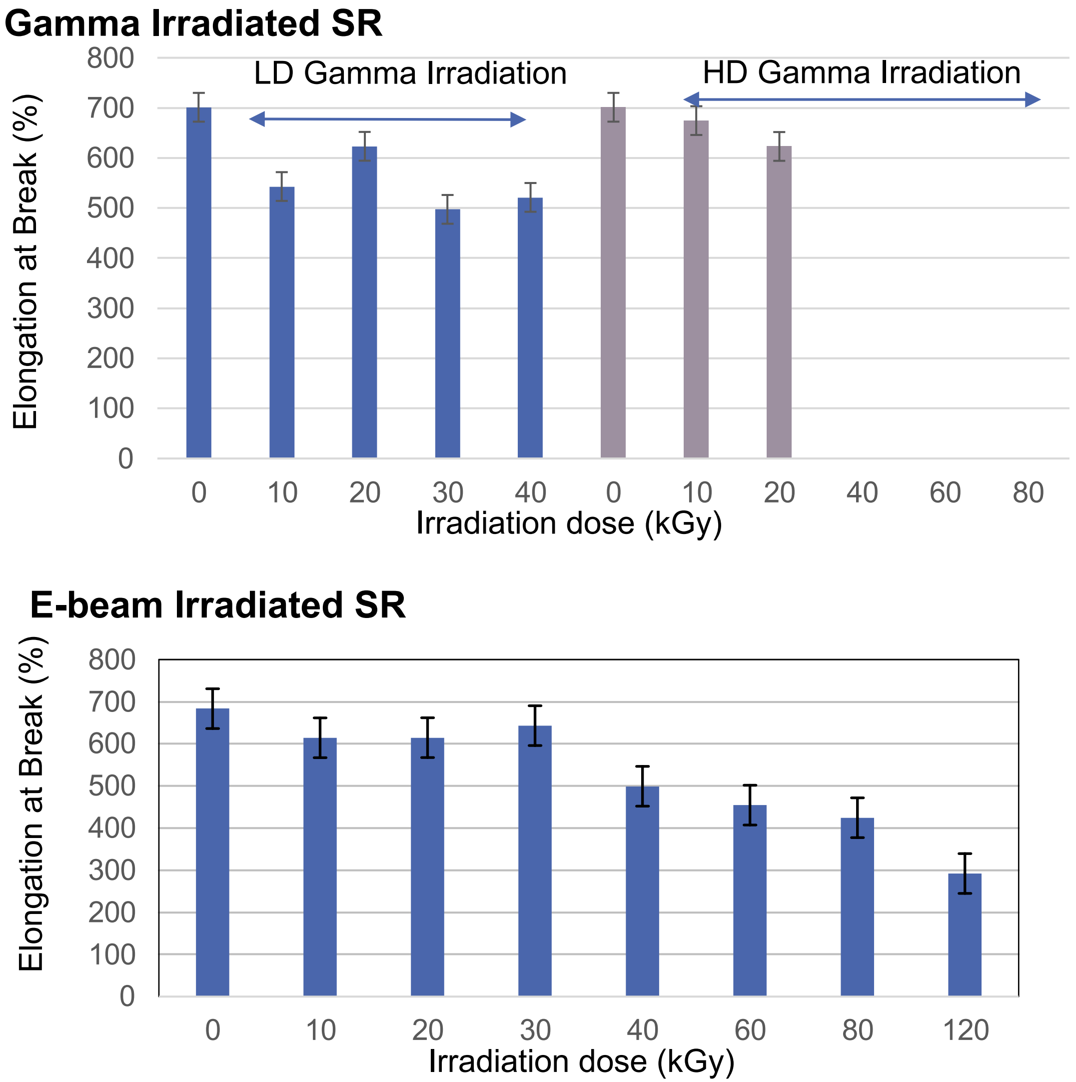


Fig.15. Elongation at break values of gamma and e-beam irradiated NR samples at different doses

Results (Fourier Transform Infrared Spectroscopy (FTIR) Analysis for NR)

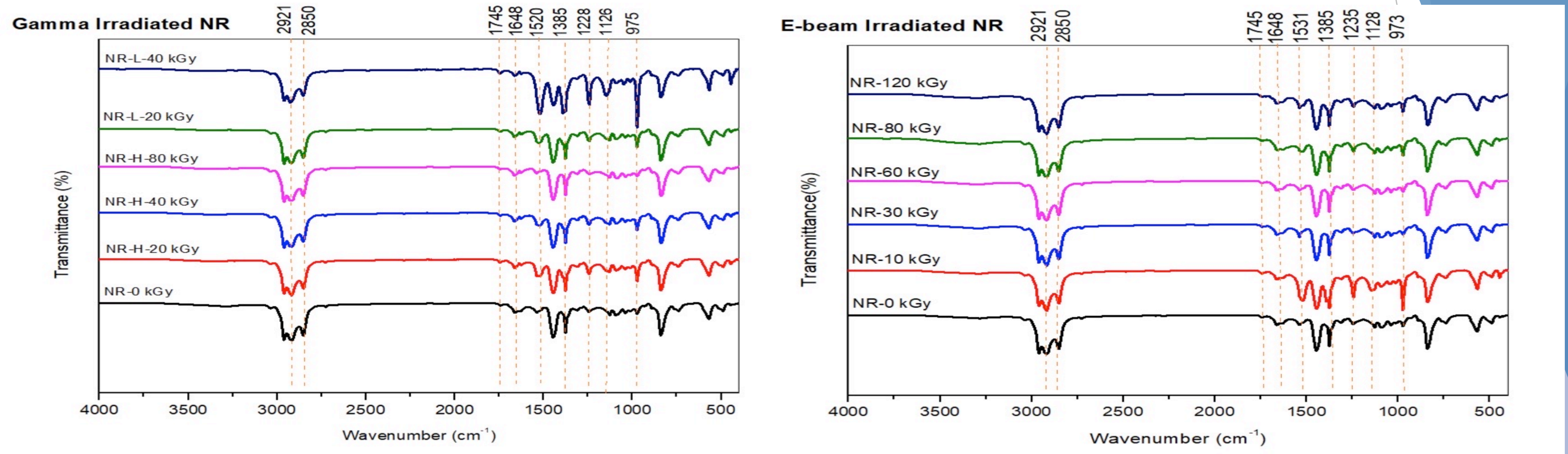


Figure 16. FTIR spectra of gamma and e-beam irradiated NR samples at different doses

For both modalities, changes in the transmittance peaks were observed at 1520-1531 cm^{-1} N-O ring stretching vibrations, at 1235 cm^{-1} and C-H stretching below 1000 cm^{-1}.

Both gamma and e-beam irradiated NR samples show their characteristic peaks at around 1385 cm^{-1} for O-H bending, 1745 cm^{-1} C=O stretching, 2921cm^{-1} $–CH_2$ asymmetrical stretching, 2850 cm^{-1} $-CH_2$ symmetrical stretching vibrations.

Results (Fourier Transform Infrared Spectroscopy (FTIR) Analysis for SR)

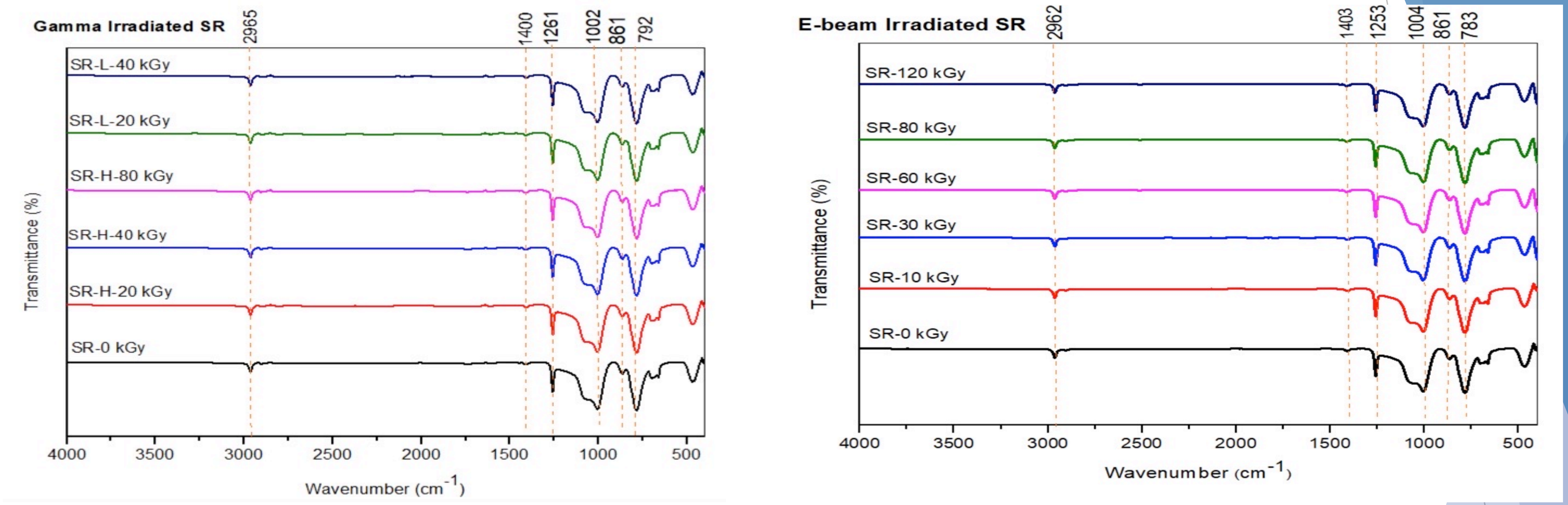
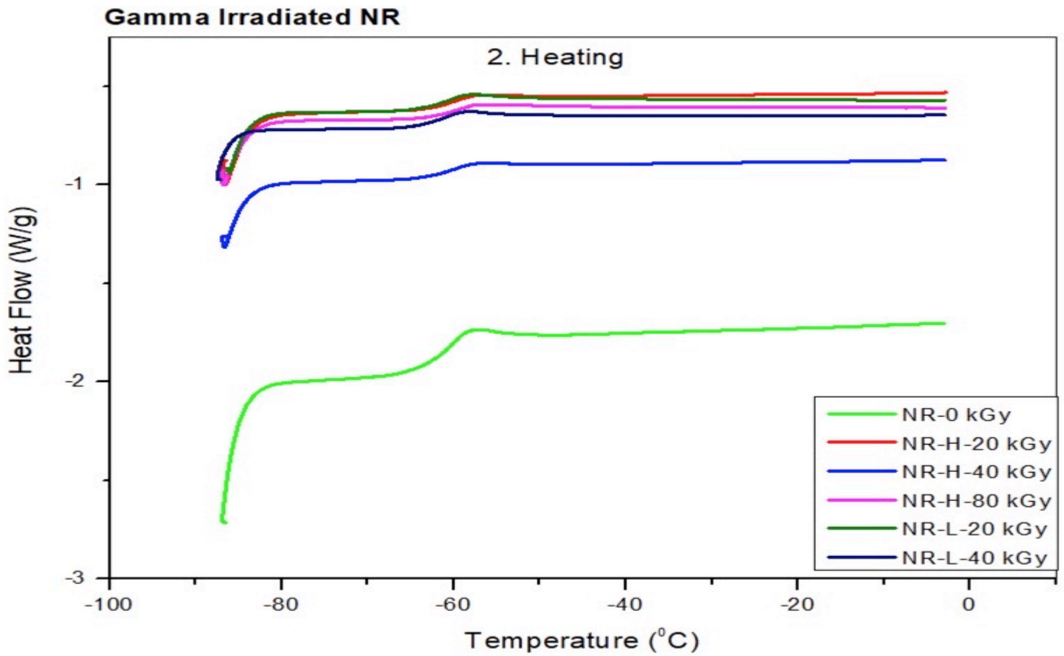


Figure 17. FTIR spectra of gamma and e-beam irradiated SR samples at different doses

Analysis of the spectrum of non-irradiated SR shows its characteristic peaks at around 2962 cm^{-1} for CH_3 stretching, 1400 cm^{-1} for $–CH_2$- rocking, 864 cm^{-1} rocking of Si-CH_3, and at 1002 cm^{-1} for Si-O-Si vibration.

FTIR spectra of the samples show that the chemical structure of the SR samples remained unchanged after irradiation.

Results (Differential Scanning Calorimetry (DSC) Analysis for NR)



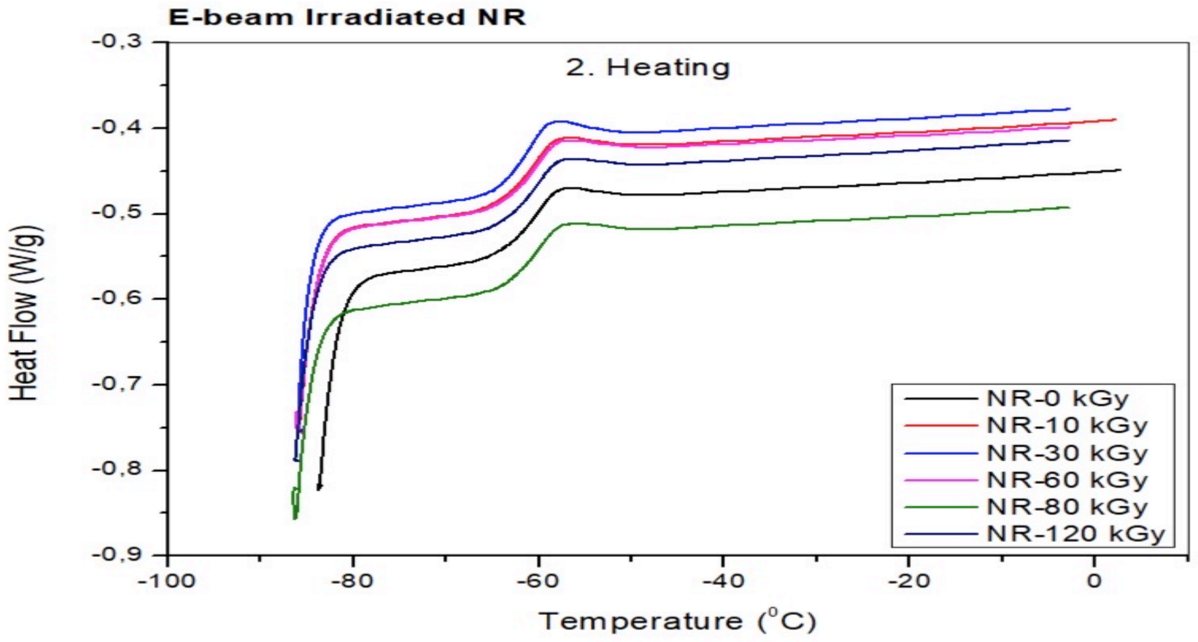
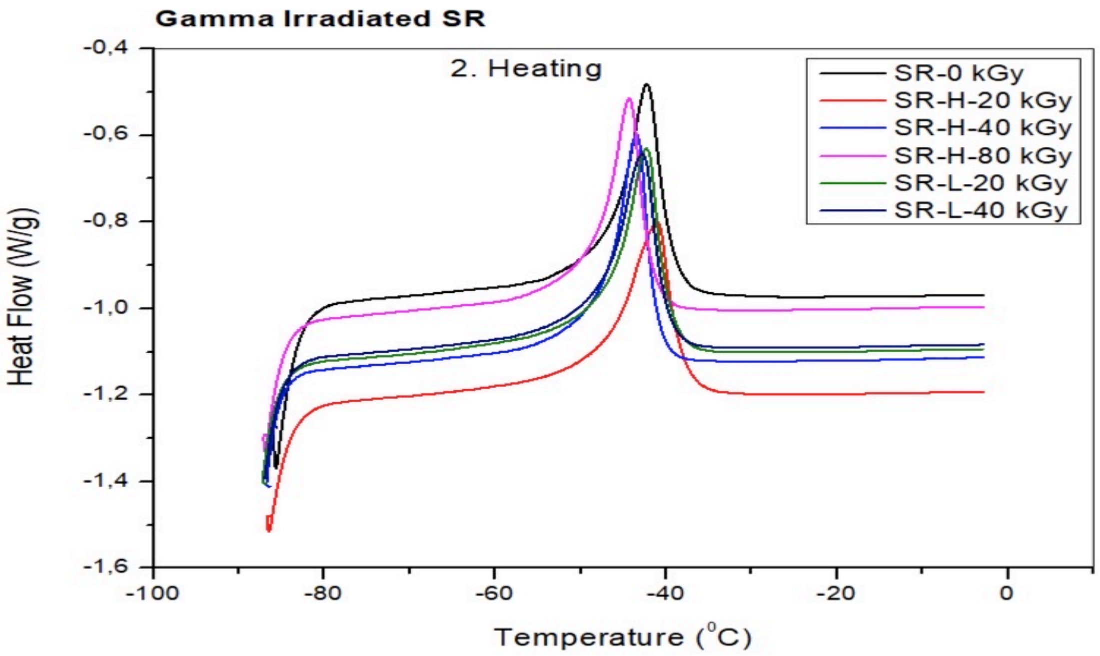


Figure 18. DSC plots of gamma and e-beam irradiated NR samples at different doses by heating from -90°C to 0°C

Gamma Irradiated NR Samples	T_g (°C)
NR-0 kGy	-60,62
NR-H-20 kGy	-59,97
NR-H-40 kGy	-59,99
NR-H-80 kGy	-59,64
NR-L-20 kGy	-60,89
NR-L-40 kGy	-61,79

E-beam Irradiated NR Samples	T_g (°C)
NR-0 kGy	-60,84
NR-10 kGy	-61,50
NR-30 kGy	-61,72
NR-60 kGy	-60,91
NR-80 kGy	-60,53
NR-120 kGy	-60,92

Results (Differential Scanning Calorimetry (DSC) Analysis for SR)



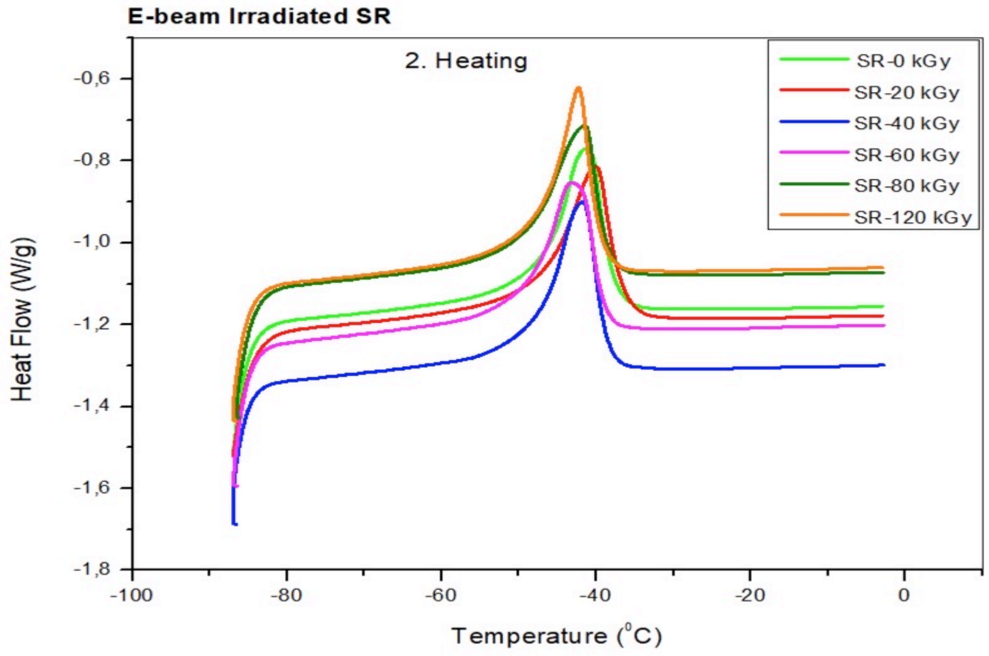


Figure 19. DSC plots of gamma and e-beam irradiated SR samples at different doses by heating from -90°C to 0°C

Gamma Irradiated SR Samples	T_g (°C)
SR-0 kGy	-42.22
SR-H-20 kGy	-41.07
SR-H-40 kGy	-43.50
SR-H-80 kGy	-44.31
SR-L-20 kGy	-42.27
SR-L-40 kGy	-42.81

E-beam Irradiated SR Samples	T_g(°C)
SR-0 kGy	-41,27
SR-10 kGy	-40,15
SR-30 kGy	-41,76
SR-60 kGy	-43,08
SR-80 kGy	-41,53
SR-120 kGy	-42,31

Results (Thermogravimetric Analysis (TGA - DTG for NR)

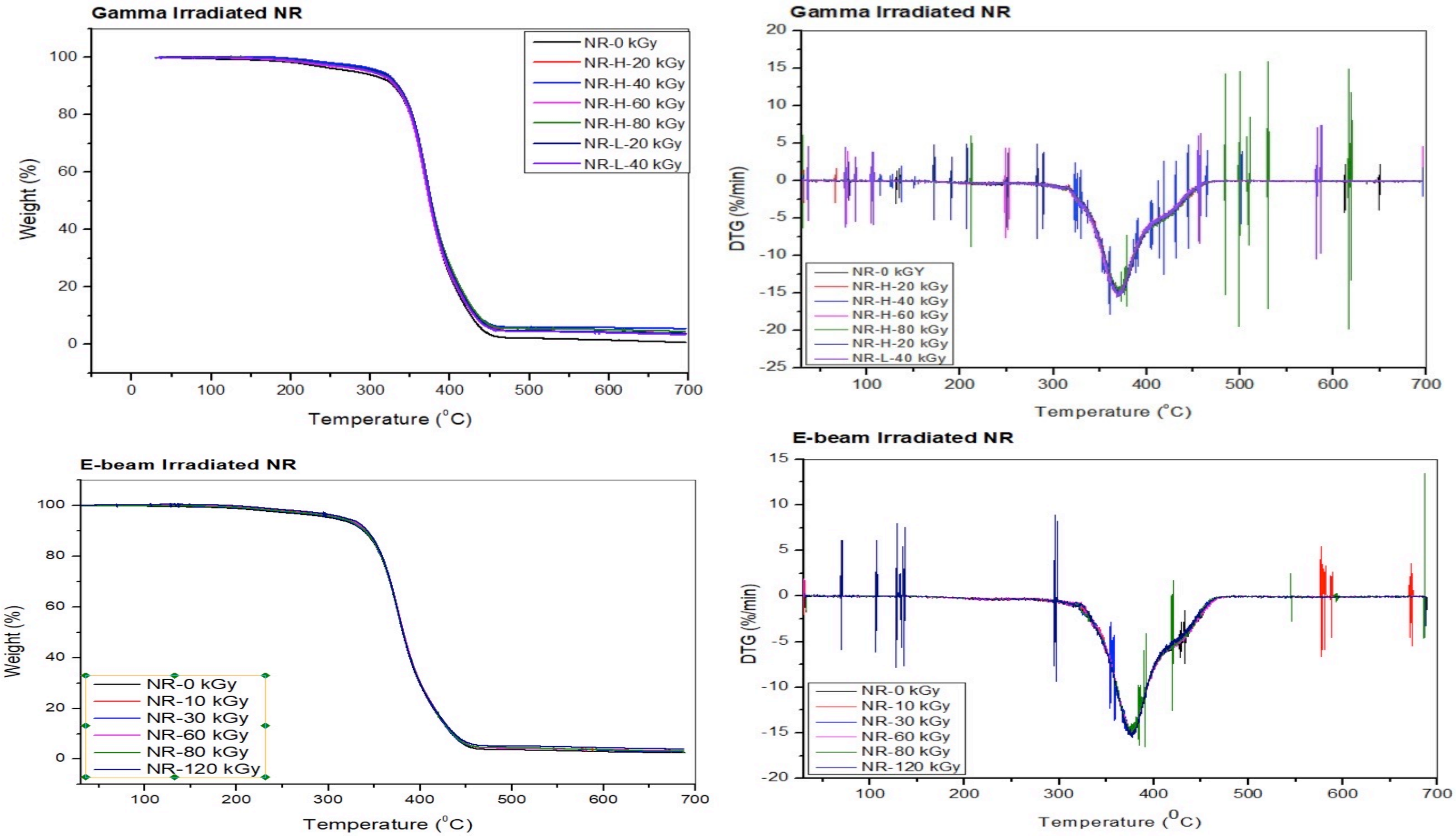


Figure 20. TGA and DTG thermograms of gamma and e-beam irradiated NR samples at different doses

Weight Loss

$320^0C - 450^0C$

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Results (Thermogravimetric Analysis (TGA - DTG) for SR)

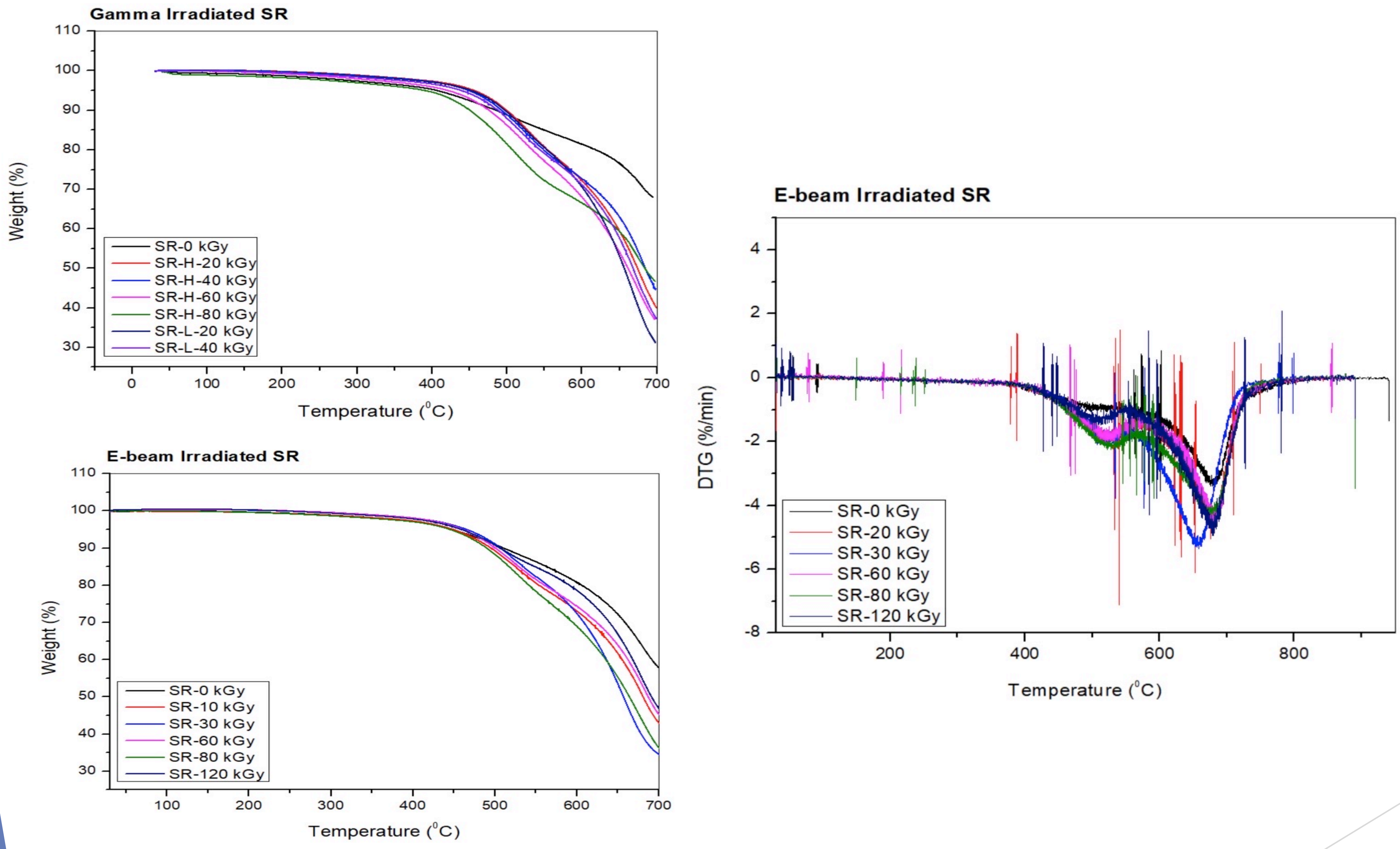


Figure 21. TGA and DTG thermograms of gamma and e-beam irradiated SR samples at different doses

Two Degradation Steps

$380^0C - 570^0C$

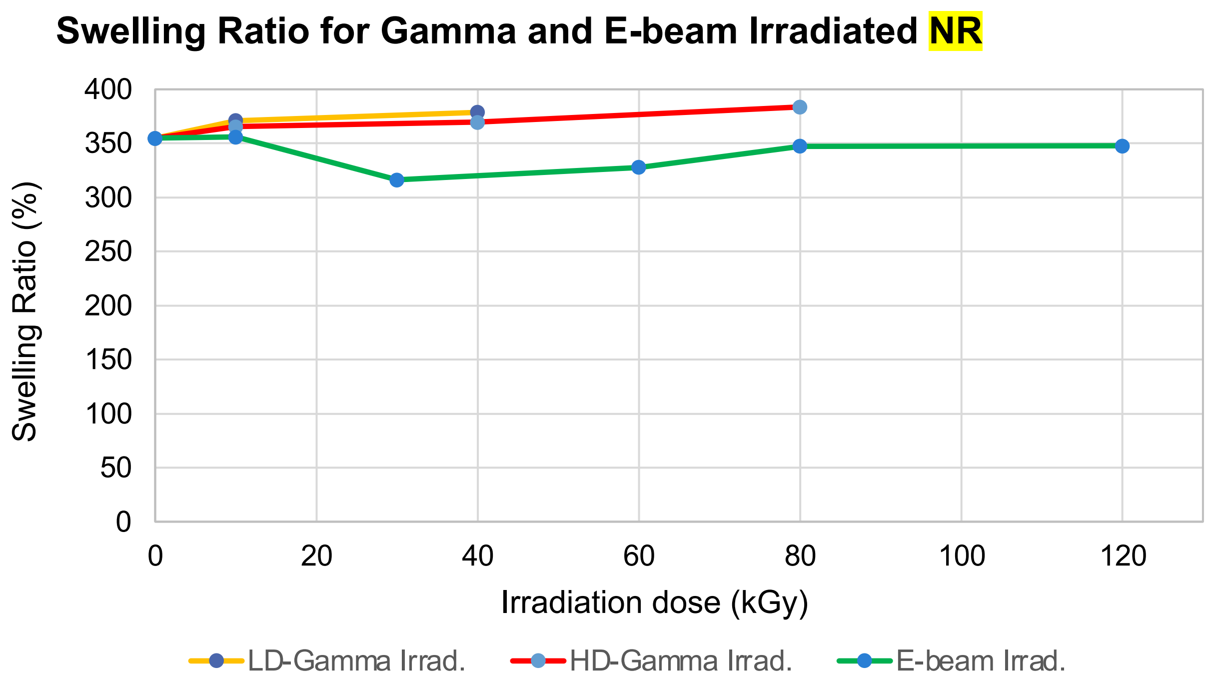
$580^0C - 750^0C$

Results (Swelling Ratio (%) for NR and SR)

Swelling Tests were performed according to ASTM D471

$$\text{Swelling Ratio (\%)} = \frac{W_f - W_i}{W_i} * 100$$

Equilibrium solvent - swelling measurements in toluene



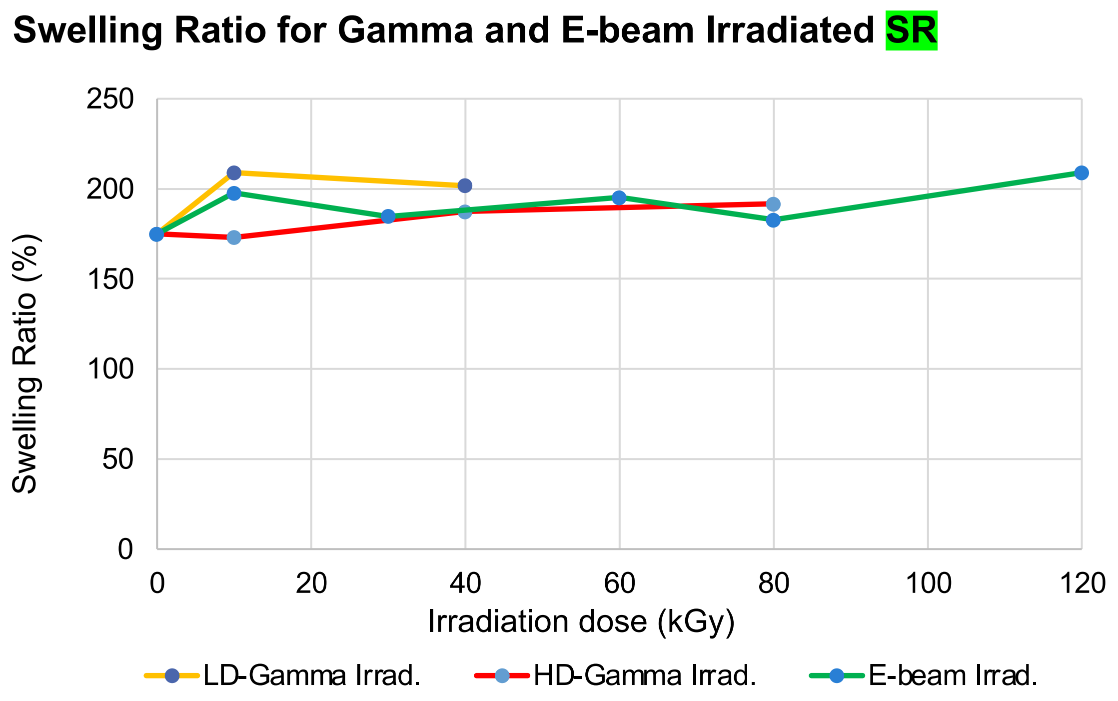


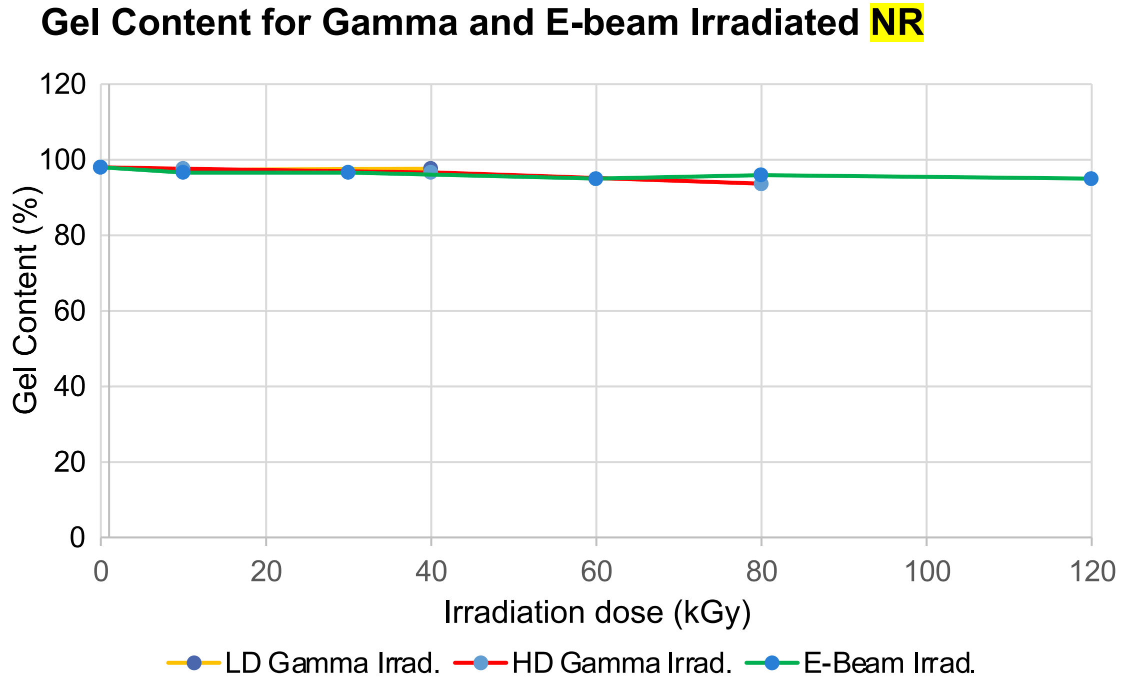
Figure 24. Swelling Ratio graphs of gamma and e-beam irradiated NR and SR samples at different doses

Results (Gel Content (%) for NR and SR)

The gel content of the samples were estimated by Soxhlet extraction method (75^{0}C - 8 h. in hexane)

$$\text{Gel Content } (\%) = \frac{wf}{wi} \cdot 100$$

Fig.26. Soxhlet Extraction Appatarus



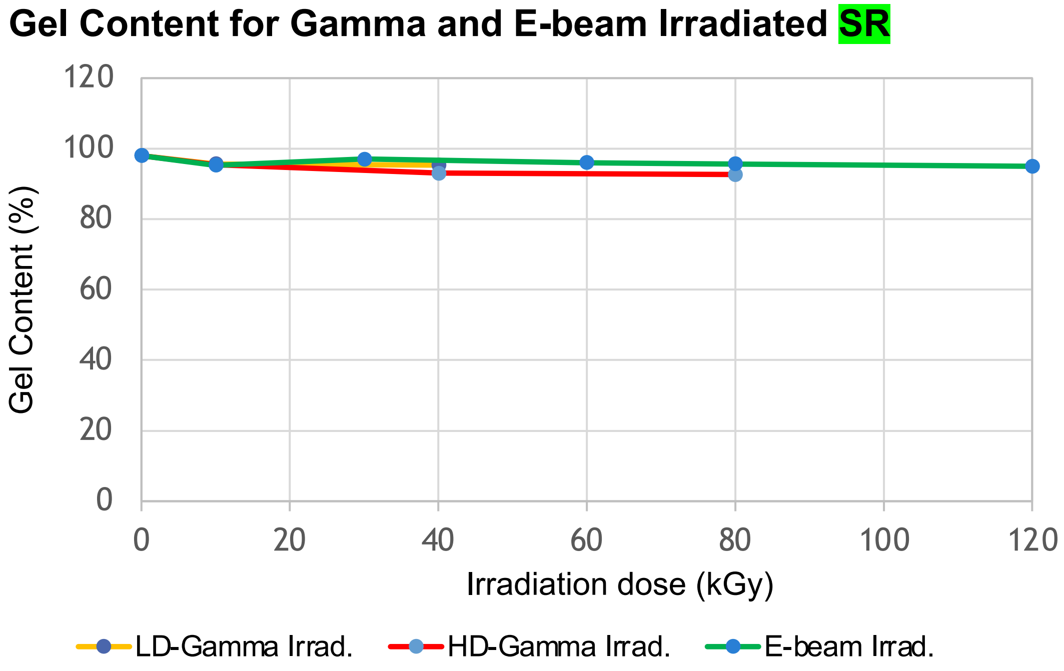


Figure 25. Gel content graphs of gamma and e-beam irradiated NR and SR samples at different doses

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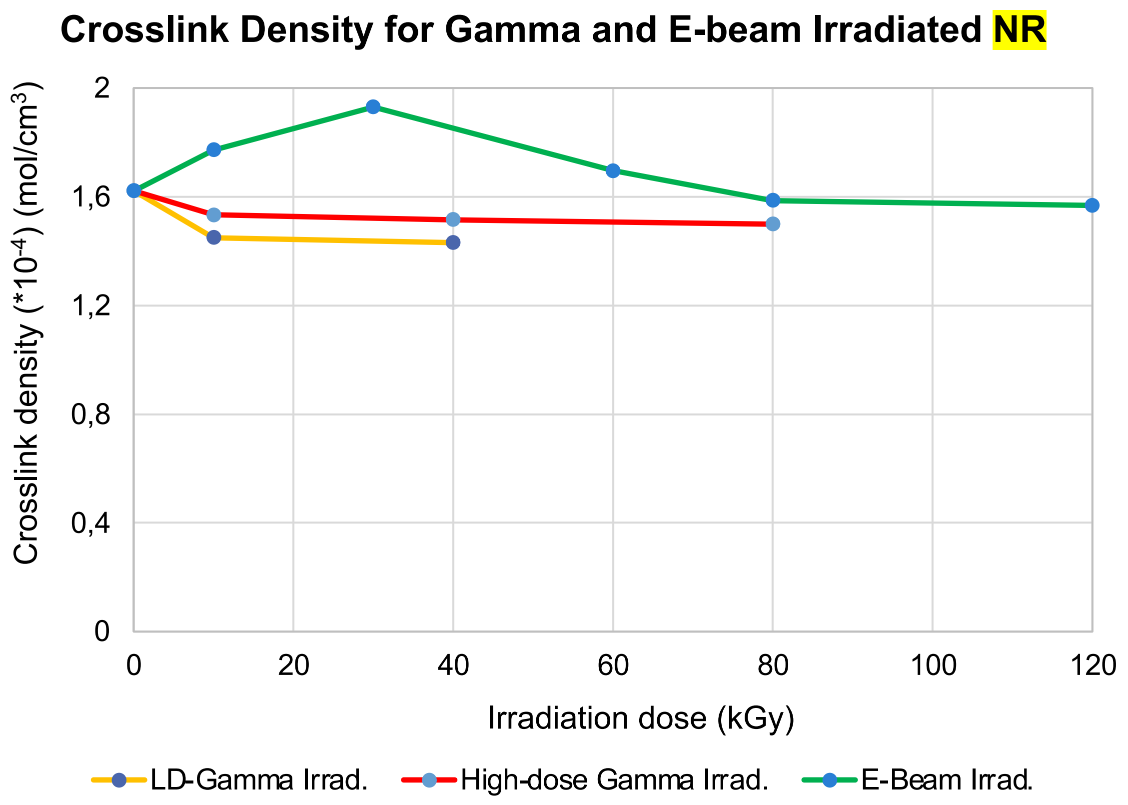
Results (Crosslink Density Calculations for NR and SR)

Crosslink density of the samples were obtained by substituting the swelling data in Flory-Rehner Eqn.

$$\nu = \frac{-\left[\ln\left(1-V_r\right)+V_r+xV_r^{2}\right]}{V_s\left(V_r^{\frac{1}{3}}-V_r/2\right)}$$



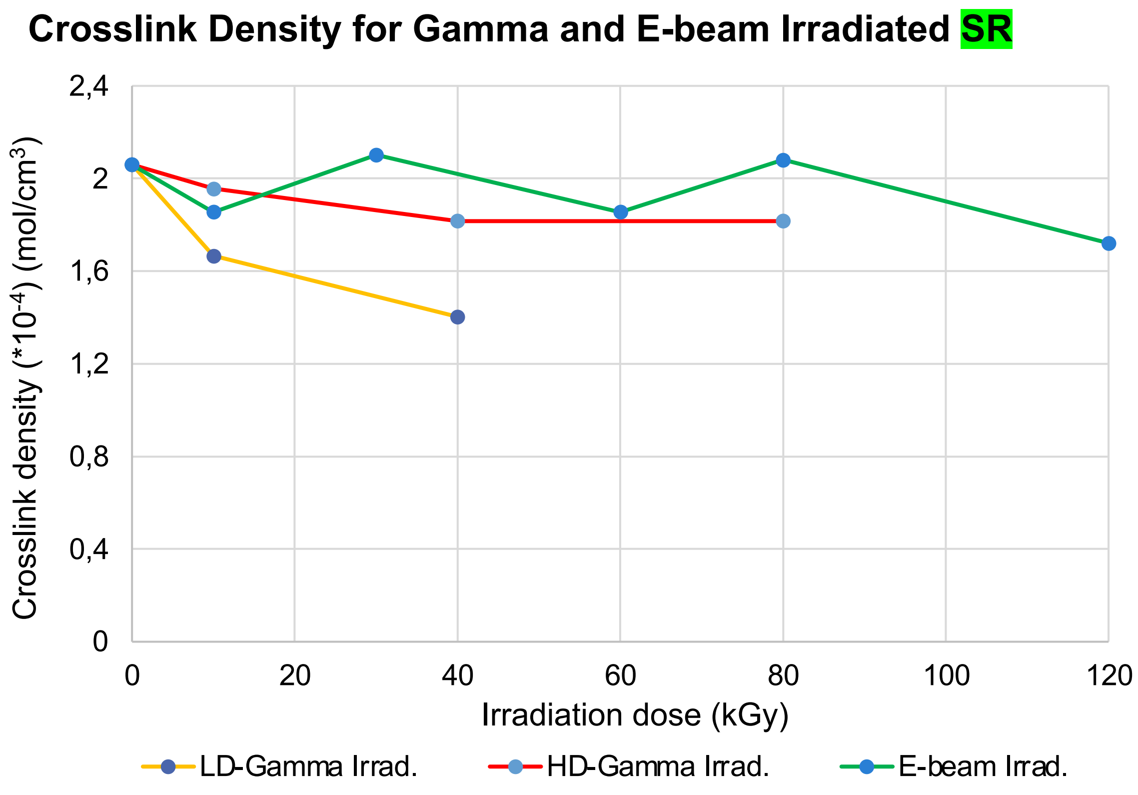


Figure 27. Crosslink density graphs of gamma and e-beam irradiated NR and SR samples at different doses

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Conclusions

- There is no critical differences in gamma and e-beam irradiations for 25 kGy, which is a sufficient dose commonly employed for sterilization.
- Gamma and e-beam irradiations produced no observable changes in the FTIR spectra of SR whereas the chemical structure of the gamma and e-beam irradiated NR samples changed with the increasing dose.
- Thermal properties of NR and SR didn't show significant changes with the increasing dose. They can be sterilized under applied conditions without any change in thermal behavior.
- LD-20 kGy of gamma and 30 kGy of e-beam irradiations have the potential to be used safely as a radiation sterilization dose for NR.
- LD-20 kGy of gamma and 20 kGy of e-beam irradiations have the potential to be used safely as a radiation sterilization dose for SR.

Ackowledgements

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THANK YOU

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