Shape Memory Acrylate Polymers Enabled by Radiation Crosslinking

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Shape Memory Polymers (SMPs)

- Shape memory polymers (SMPs): smart materials which can recover from the temporary shape to the permanent shape upon an external stimulus.
- Two types:
  - Thermoplastic SMP: polyurethane
  - Thermosetting SMP: chemically crosslinked polymers
- SMP manufacturing
  - Thermoplastic SMP: conventional processing
  - Thermosetting SMP: reactive processing

    OR post-manufacturing processing – **ionizing radiation**

Ionizing radiation

- Two competitive processes during the exposure to radiation
  - Chain scissioning
  - Crosslinking
- Charlesby–Pinner equation

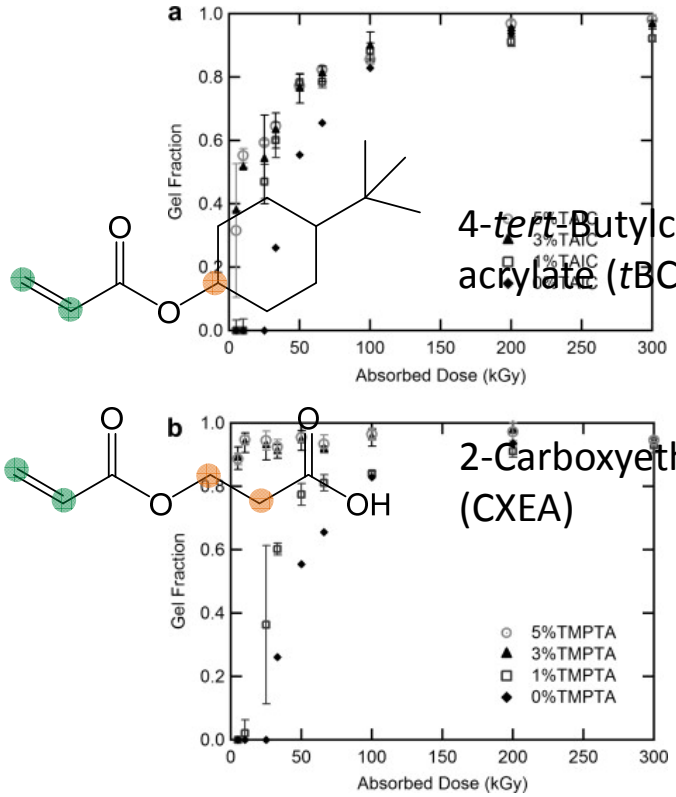
$$s + s^{\frac{1}{2}} = \frac{p_0}{q_0} + \frac{1}{q_0 \mu_1 d}$$

  - s: sol fraction
  - p_0: degradation density
  - q_0: crosslinking density
  - d: radiation dose
  - μ_1: starting molecular weight

Earlier work on radiation on acrylate polymers

- Previously, we have studied several acrylate polymer systems

1. Neat poly(methyl acrylate) (PMA) and its blends with sensitizers (TMPTA and TAIC)

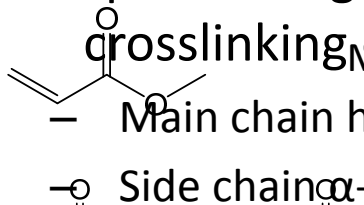


4-*tert*-Butylcyclohexyl acrylate (*t*BCHA)

2-Carboxyethyl acrylate (CXEA)

Figure 1. Gel fraction as a function of radiation dose for PMA blended with increasing concentrations of a) TAIC; b) TMPTA.

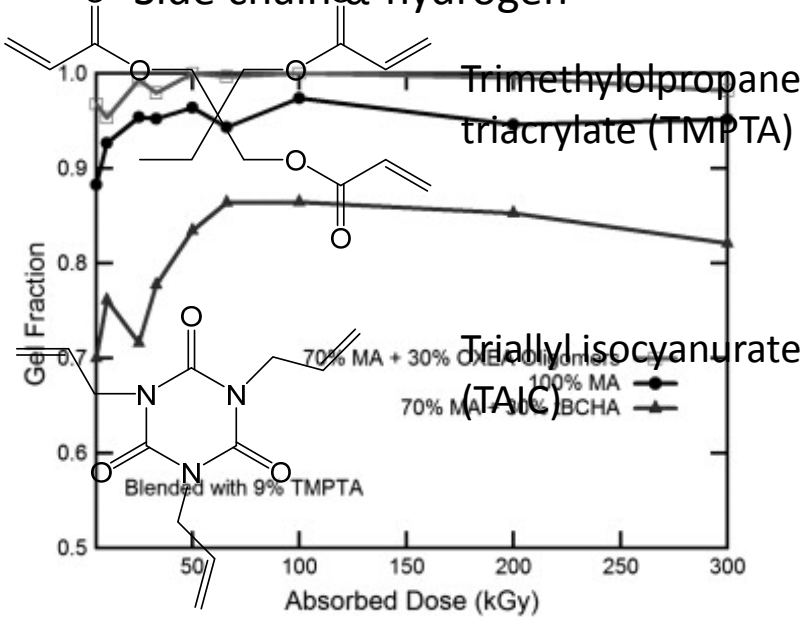
2. PMA copolymers: to study specific targets of radiation crosslinking of acrylates



Methyl acrylate (MA)

– Main chain hydrogen

– Side chain α-hydrogen



Trimethylolpropane triacrylate (TMPTA)

Triallyl isocyanurate (TAIC)

Figure 1c. Gel fraction as a function of radiation dose

Voit, W.; Ware, Y.; Gall, K. Polymer 2010, 51(15), pp. 3551–3559

Earlier work on radiation on acrylate polymers

3. MA-IBoA copolymer and PLA:

To study radiation temperature effects

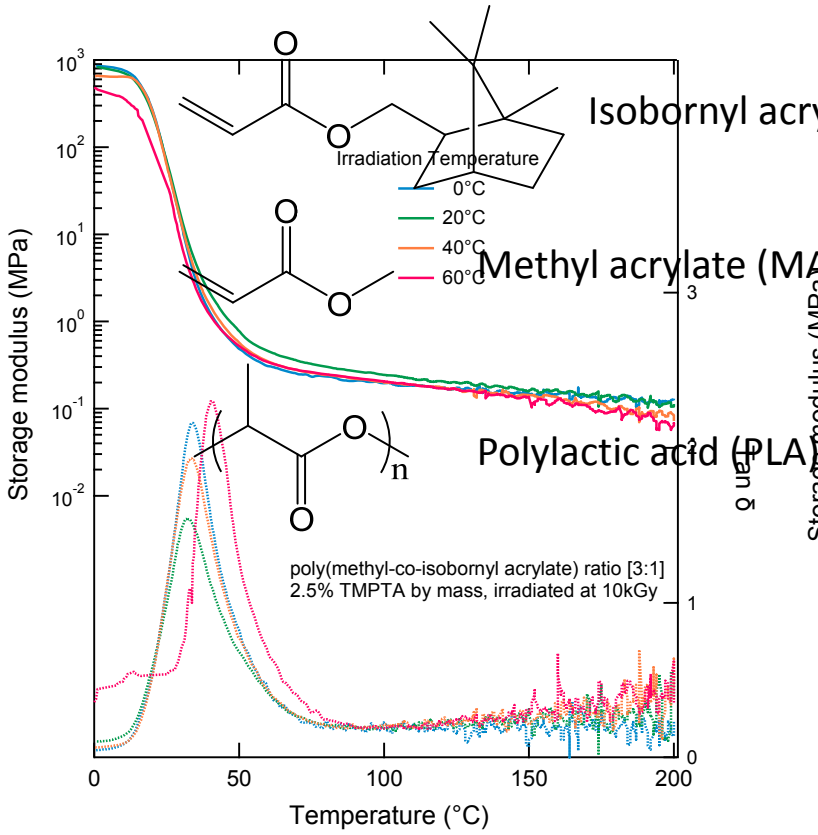


Fig.2 DMA curves of copolymers of 75% MA and 25% IBoA

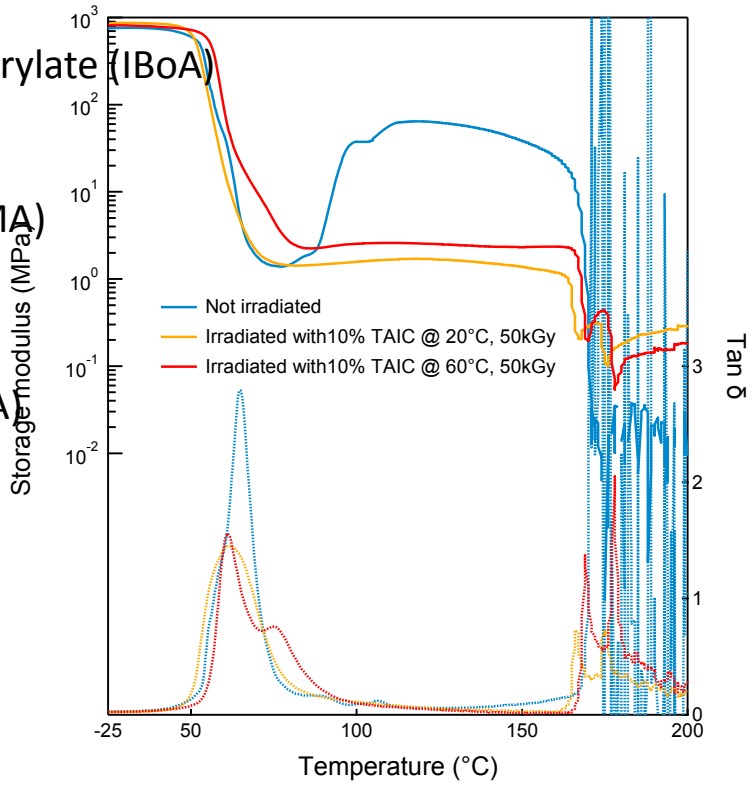


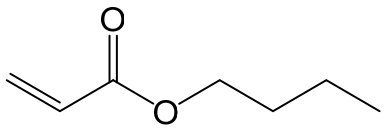
Fig.3 DMA curves of PLA blends

Shaffer, S.; Yang, K.; Vargas, J.; Di Prima, M.A.; Voit, W. Polymer 2014, 55(23), pp. 5969–5979

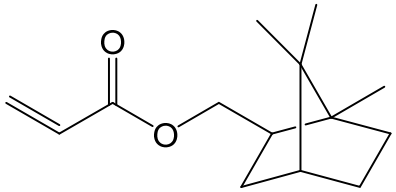
Continuing work

- Acrylate copolymer synthesis

	BuA	IBoA
Sample #1 composition (wt%)	25	75
Sample #2 composition (wt%)	33	67

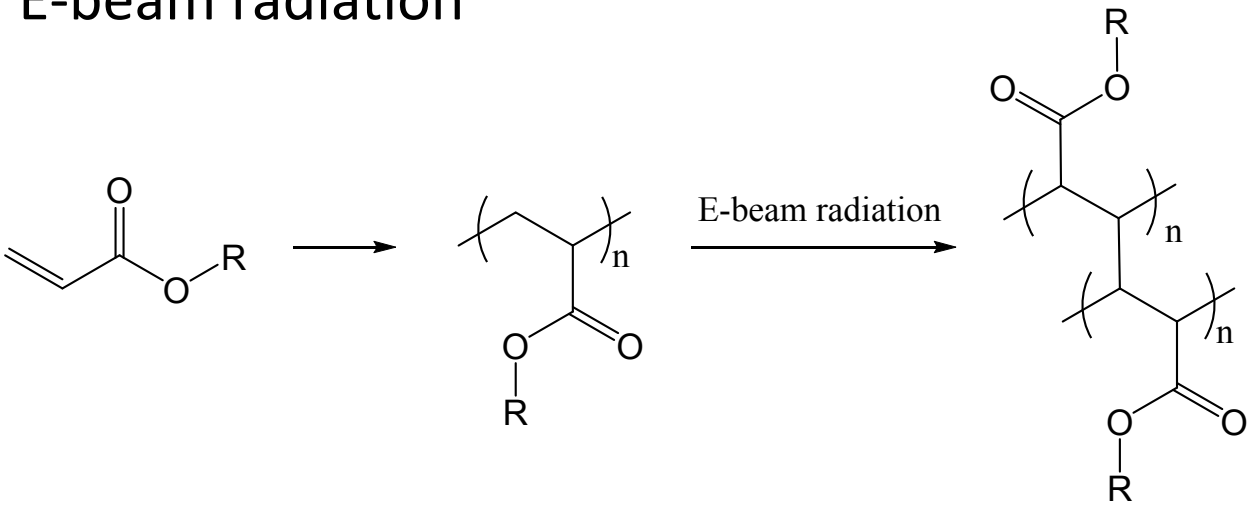


n-Butyl acrylate (BuA)



Isobornyl acrylate (IBoA)

- E-beam radiation



Thermogravemetric Analysis (TGA)

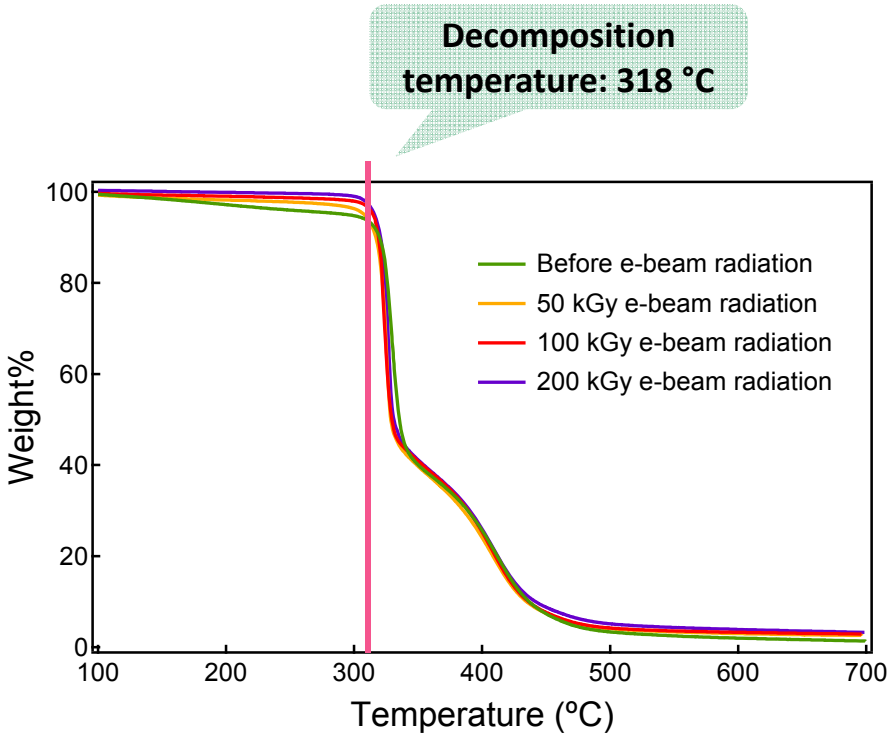


Fig.4 TGA curves of copolymers of 25% BuA and 75% IBoA

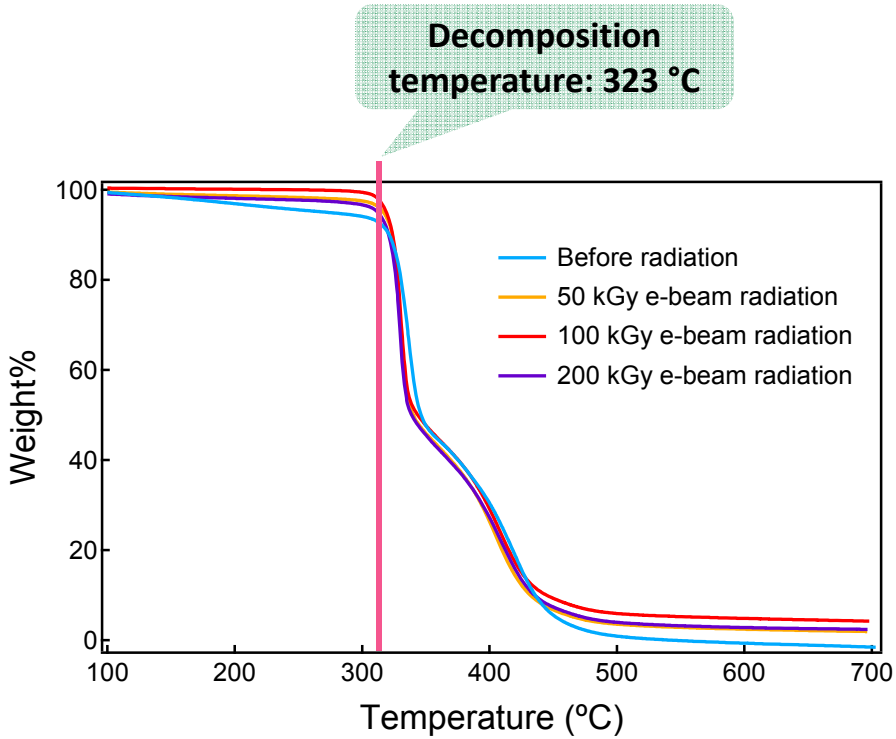


Fig.5 TGA curves of copolymers of 33% BuA and 67% IBoA

- No obvious difference in thermal decomposition temperature before and after irradiation
- Radiation did not change samples' thermal decomposition temperatures but improved the homogeneity.
- Crosslinking density may be low, if any.

Solvent test

- All samples were soaked in chloroform at room temperature for a week.
- None of the irradiated samples dissolved – all swelled in chloroform
- All irradiated samples were lightly crosslinked

Sample composition	Dose (kGy)	Swelling rate in chloroform (%)
25%BuA-75%IBoA	50	–
	100	2118.52
	200	1571.39
33%BuA-67%IBoA	50	–
	100	1571.39
	200	2078.00

*Samples irradiated at 50 kGy: swelled samples difficult to separate out from solvent

Differential Scanning Calorimetry (DSC)

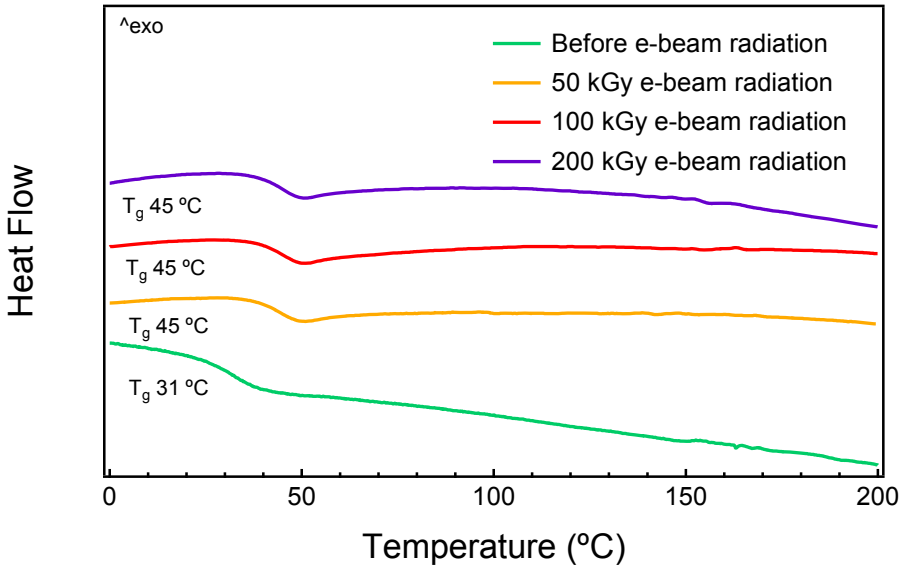


Fig.6 DSC curves of copolymers of 25% BuA and 75% IBoA

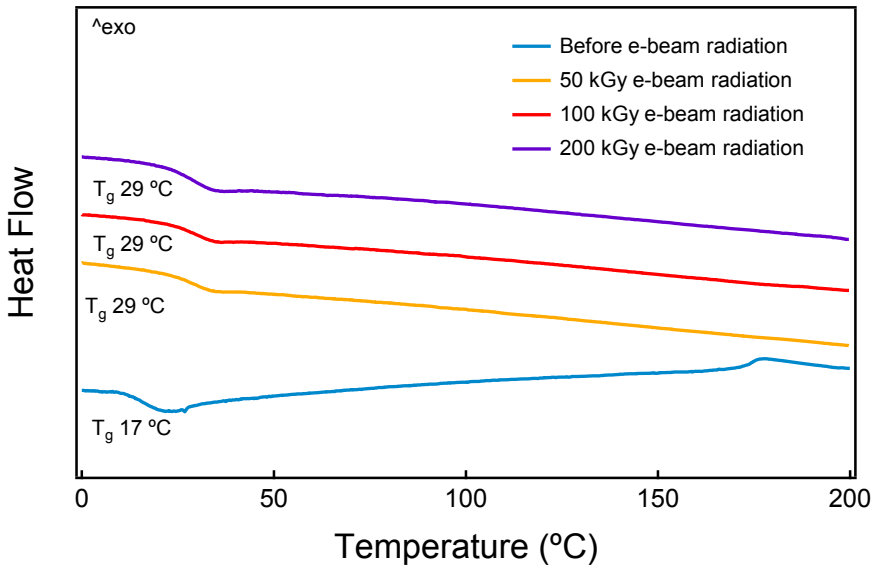


Fig.7 DSC curves of copolymers of 33% BuA and 67% IBoA

- All irradiated samples showed higher glass transition temperatures

Dynamic Mechanical Analysis (DMA)

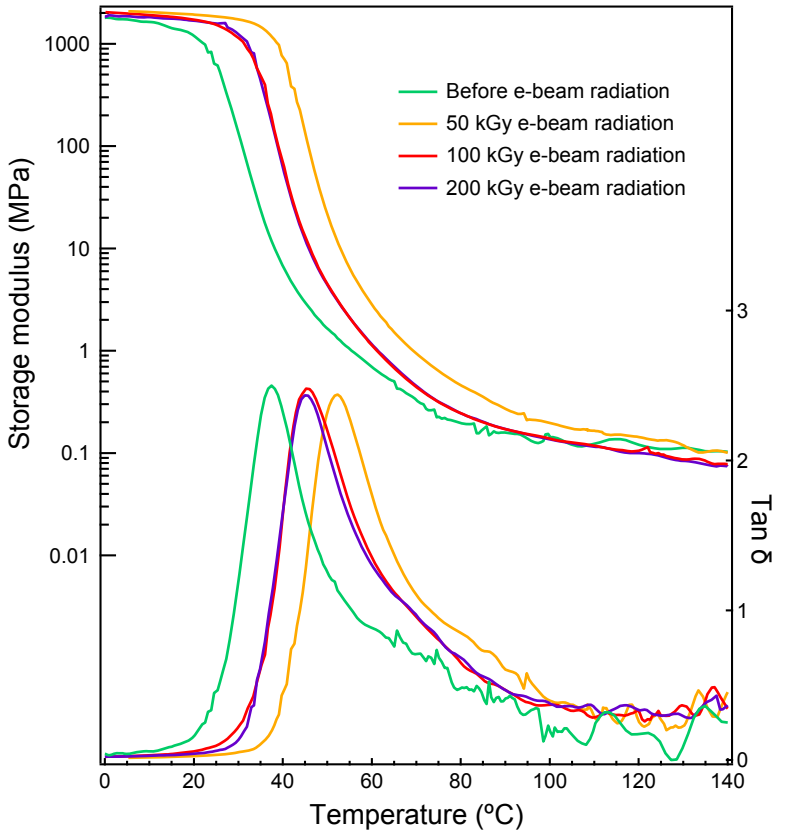


Fig.8 DMA curves of copolymers of 25% BuA and 75% IBoA

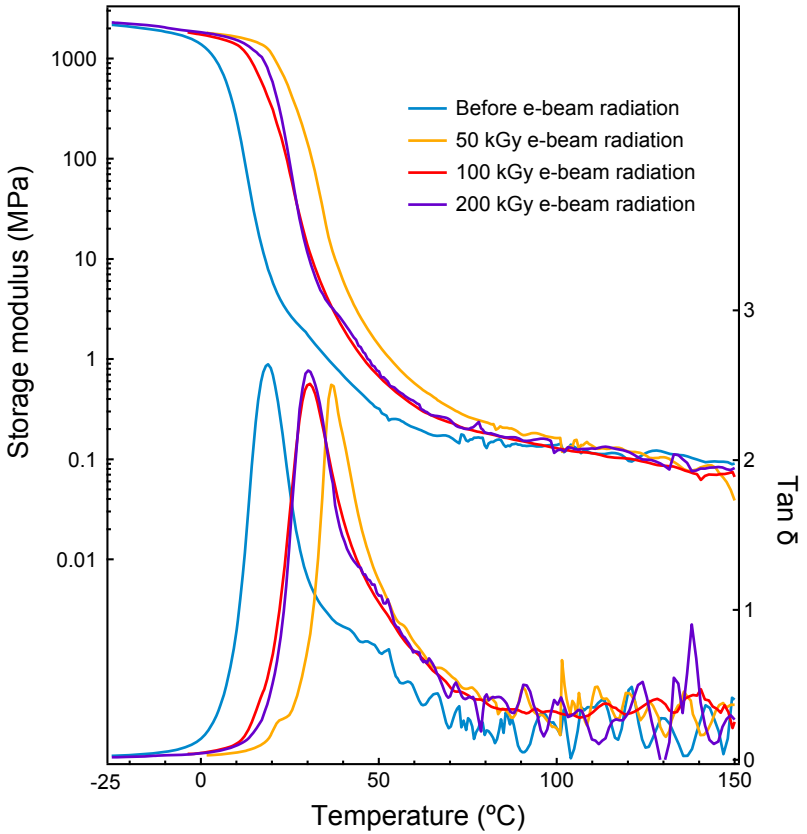
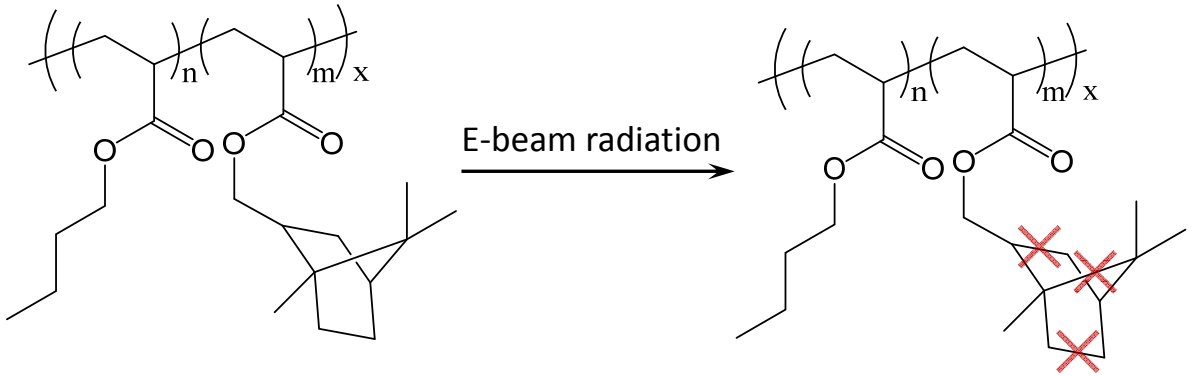


Fig.9 DMA curves of copolymers of 33% BuA and 67% IBoA

- In DMA, samples irradiated at 50 kGy showed the highest T_g
- All rubbery modulus of irradiated samples dropped lower than 100 kPa – lightly crosslinked

Conclusion and future work

- BuA-IBoA copolymers were crosslinked when exposed to e-beam radiation at 50, 100, and 200 kGy, and the crosslinking density was low
- TGA showed no difference in thermal decomposition temperature between un-radiated and irradiated samples
- DSC showed all irradiated samples have similarly higher T_g, while DMA showed samples irradiated at 50 kGy have the highest T_g



- Future work:
  - Investigate the specific targets of radiation crosslinking of BuA-IBoA copolymers
  - Employ TGA-MS (mass spectroscopy) to study the side groups of irradiated polymers, in order to further investigate how the radiation at 100 and 200 kGy affect the samples' glass transition temperatures

Reference

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