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The Effects of Irradiation Technologies on Some Polymers commonly used in SUDs

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"The effects of irradiation technologies on some polymers commonly used in SUDs"

Olivier VRAIN, Radiation Technical Manager, UK & Ireland AST

ECI Conference: 19th October 2015

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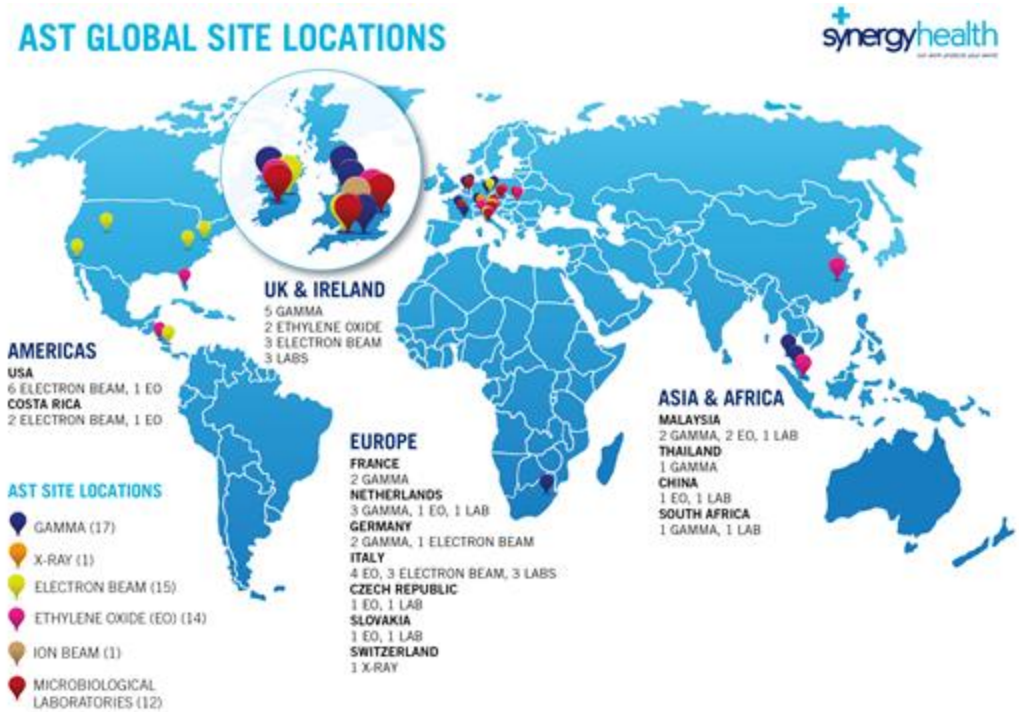
Synergy Health is a global outsourcing provider to the healthcare sector and other related markets.

There are six core parts of the business:

- **Hospital Sterilisation Services;**
- **Applied Sterilisation Technologies;**
- **Healthcare Solutions;**
- **Linen Management Services;**
- **Laboratory Services and Pharmaceutical Laboratories.**



Presenter:

Olivier Vrain, Radiation Technical Manager UK & Ireland

- Worked within the Veterinary, Pharmaceutical and Medical Device industry since 2002,
- Working with Synergy Health since 2006,
- Leader of the Synergy Health Global Radiation Technical Advisory Board.
- Active member of the ASTM E61 committee on dosimetry
- Active member of the Panel on Gamma and Electron irradiation

Introduction: Ionising Radiation Type Studied

Most medical devices must be sterilised prior to be used.
Sterilisation methods available are:

- Ionising Radiation,
- Gas Technologies (EO, mixed gaz – EO/CO^2, Plasma),
- Steam.

When opting for ionising radiation as sterilisation method of choice, the following fact must be known and understood:

"Ionising radiation can cause significant damage and degradation to polymers due to the energetic secondary electrons released from the primary irradiation event. "

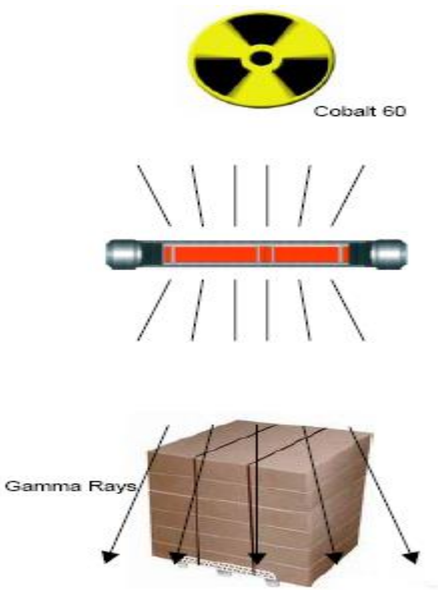
Type of ionising radiation available and commonly used for the sterilisation of medical devices (SUDs):

- Gamma Radiation (Cobalt 60),
- Beta Radiation (Electron Beam),
- X-ray Radiation (Electron Beam converted to X-Ray).

Comparison Between Gamma Ray & E-Beam Irradiation

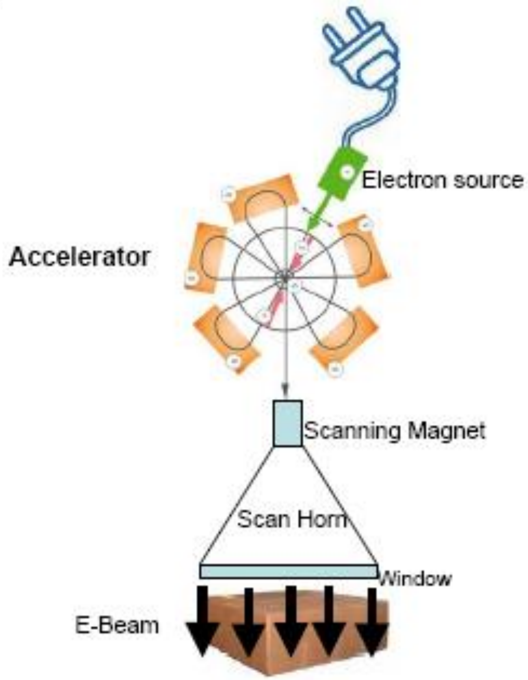
γ-irradiation

- Source emits in all directions
- Large inventory of material irradiated at any one time
- Moderate dose rate



EB-irradiation

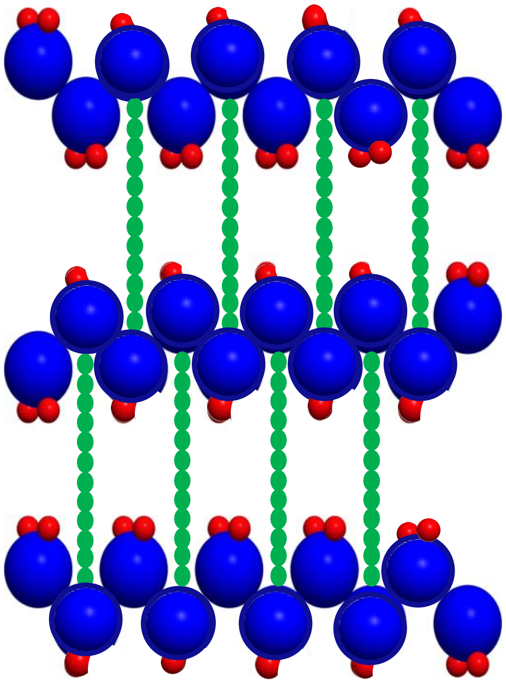
- Beam highly concentrated
- Small volume of material irradiated at any one time
- High dose rate

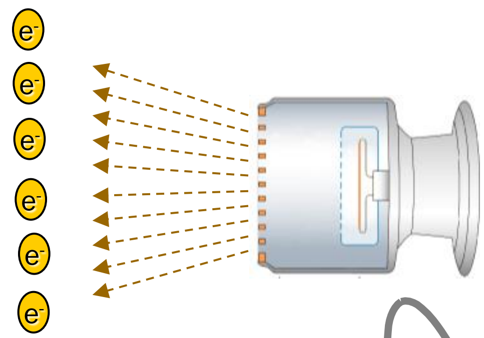


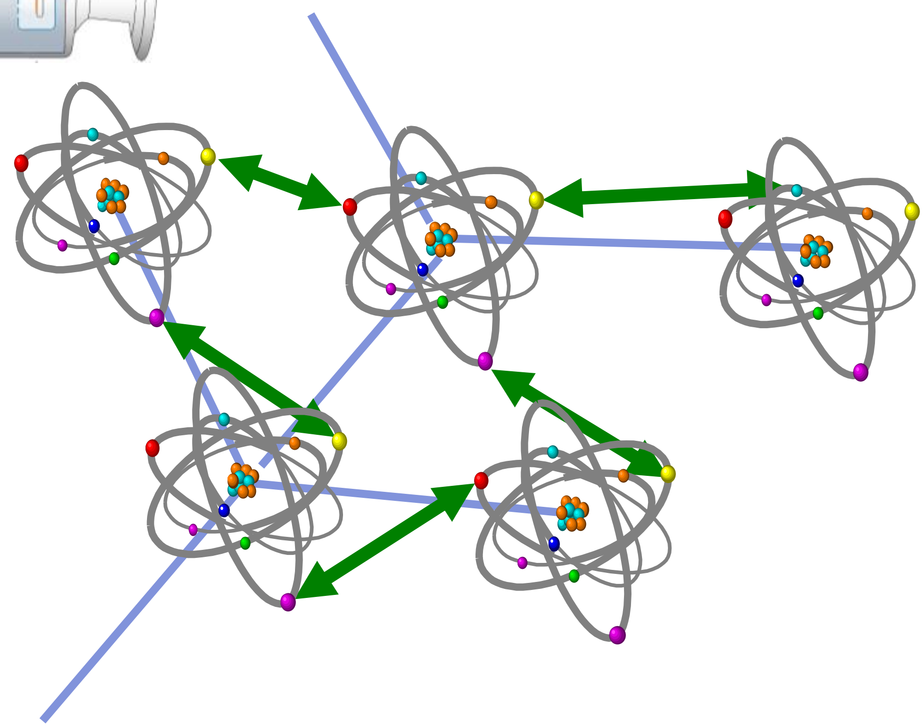
Comparison between Gamma Ray & E-Beam Irradiation equipment used

	Gamma Radiation	E-Beam
Source	^{60}Co	3 - 12 MeV
Dose Rate	Circa 8 kGy / hr	1 – 100 kGy / sec or 360,000 kGy / hr
Penetration	50 cm of unit density	5 cm of unit density
Time	2 – 6 hours	Approx 1 minute

Effect of Ionising Radiation on Polymers: Crosslinking



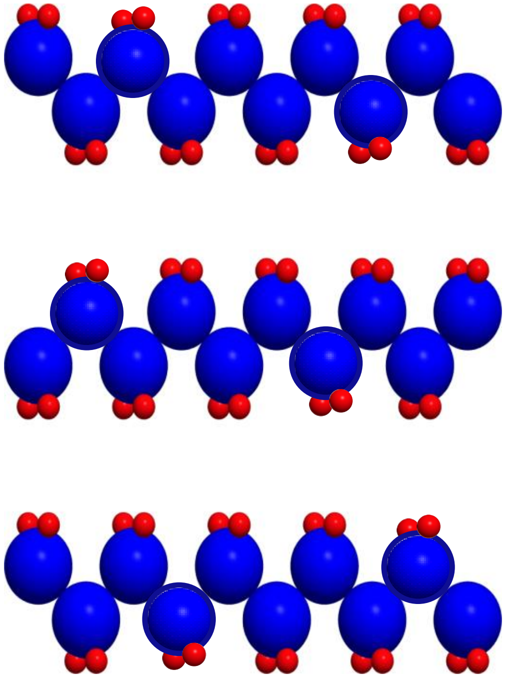


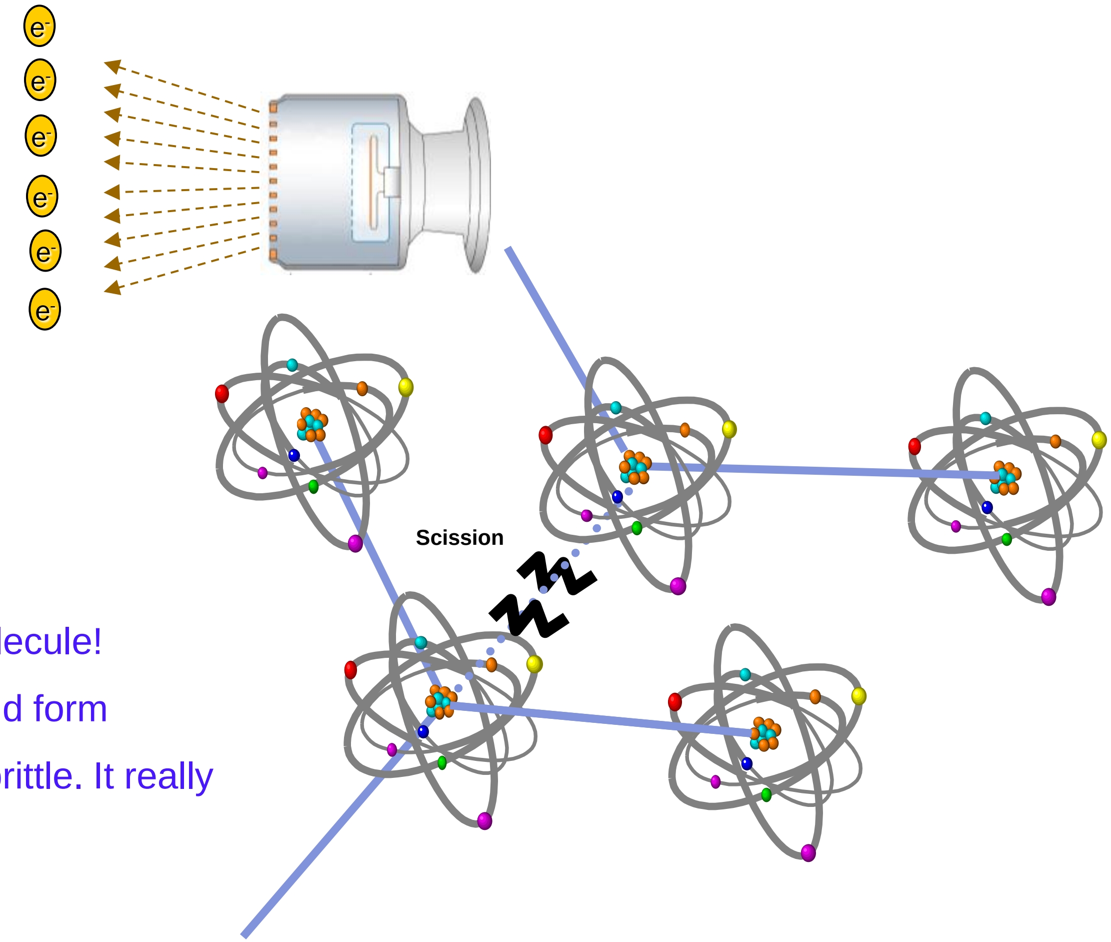


- Extra bonds have now been created within the molecule!
- This can make the molecule stronger. It can also leave a memory of its shape and form
- It can also make the molecule more brittle or less. It really does depend on the material.

Effect of Ionising Radiation on Polymers:

Chain Scission





- Bonds could be broken within the molecule!
- It can leave a memory of its shape and form
- It can also make the molecule more brittle. It really does depend on the material.

Example of ionising radiation effect on un-stabilised polymers

Cross-linking: towards infinite networks,

Formation of high molecular-weight compounds,

e.g. Polyethylene (PE), Ethylene Vinyl Acetate (EVA), Natural Rubber, Polyvinylalcohol (PVA), Polyvinylchloride (PVC).

Degradation: Chain scission (breaking of molecular chain)

Formation of low molecular-weight compounds,

Hydrogen formation.

e.g. Polyproplylene (PP), Polymethymetacrylate (PMMA),

Polytetrafluorethylene (PTFE), Polyoxymetacrylate (POM), Cellulose.

Some polymers are **"almost" not affected** " by radiation:

e.g. Polystyrene (PS), Polyethylene Terephthalate (PET), Acrylonitrile Butadiene Styrene (ABS), Polycarbonate (PC).

STUDIES of polymers commonly used in SUDs.

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SURVEY
of SUDs Primary Manufacturer/Designer

Would you consider entering a 3 way partnership study(ies)?

NOT INTERESTED

What polymers do you commonly used in your SUD's and associated packaging?

- Low Density Polyethylene (LDPE),
- Polypropylene (PP),
- Poly (ether-block-amide) thermoplastic elastomers (PEBA),
- Polytetrafluoroethylene (PTFE) or Teflon

Selection of Polymers & Studies Objectives

Polymers selection:

- LDPE (un-stabilised), LDPE is used in the industry for its crosslinking properties.
- PP (un-stabilised), Polypropylene (PP) is one of the most widely used plastics throughout industry as it is the polymer of choice for many applications due to properties such as high tensile strength, high modulus, hardness, chemical resistance and excellent heat resistance
- PEBA (PEBAX 6333 SA01 - medical grade poly (ether block amide) virgin polymer manufactured by Arkema) PEBAX is mainly used in the medical device industry as they offer valuable properties such as elasticity and thermal stability at body temperatures

Objectives of Studies :

1. Understand the effect of Gamma and E-Beam irradiation on the mechanical, structural, chemical and thermal properties.
2. Study to be completed within the sterilisation dose range.

This was completed in order to gain:

- To increase our knowledge on the effect radiation has on these polymers, and
- To potentially attempt to identity method/techniques that would minimised any detrimental effects identified

Low Density Polyethylene (LDPE)

Samples Preparation

Material

Virgin low density polyethylene manufactured by ExxonMobil Chemical Company.

- Melt flow index (MFI): 0.55g/10min under loading of 2.16kg at 190°C,
- Density: 0.929g/cm
- Melt temperature: 114°C.

Injection moulding and packaging

An Arburg injection moulding machine was utilised in manufacturing type IV ASTM D638 testing specimens.

Sample preparation played a significant role in the radiation process as this controlled the uniformity of the irradiation dose on the samples.

Low Density Polyethylene (LDPE) – Cont.

Samples Irradiation

Electron beam irradiation

Accelerator Type: Mevex high energy electron beam Linac Accelerator (10MeV unit, 20KW)
Irradiation Doses: 25, 50, 75, 100, 150, 200 and 400kGy.
Dose rate: approx. 12.5kGy per pass on each side.
Irradiation Conditions: Room temperature in the presence of air
Note that non-irradiated samples served as the baseline for each of the test.

Gamma ray irradiation

Accelerator Type: A gamma irradiator using a cobalt 60 energy source (circa 3.5 MCi)
Irradiation Doses: 25 and 200kGy.
Dose rate: approx. 8 kGy per hour.
Irradiation Conditions: Room temperature in the presence of air
Note that non-irradiated samples served as the baseline for each of the test.

Low Density Polyethylene (LDPE) – Cont.

Characterisation Tests Completed

- ***X-Ray Diffraction:***
  This characterisation technique is to investigate the modifications induced by irradiation such as crystallite size and relative crystallinity.

- ***Scanning Electron Microscope (SEM),***
  Study of the surface morphology.

- ***Colorimetry***
  Yellowness index to evaluate the colour change using the following equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

Where:
ΔE is expressed as the difference between the control sample and the irradiated sample colour values.
*Δ*L is the difference of Hunter *L* (black (0) to white (100)),
*Δ*a is the difference of Hunter *a* (green (-) to red (+))
*Δ*b is the difference of Hunter *b* (blue (-) to yellow (+)).

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Low Density Polyethylene (LDPE) – Cont.

Characterisation Tests Results

- ***X-Ray Diffraction:***
  X-ray diffraction studies implied that radiation crosslinking occurred without significantly affecting the material crystalline structure and degree of crystallinity. .

- ***Scanning Electron Microscope (SEM),***
  With regard to the SEM imagery, a considerable amount of degradation transpired on the surface of the material subsequent to irradiation which could be attributed to oxidation.

- ***Colorimetry***
  This characterisation technique:
  1. Revealed that both the electron beam and gamma ray processes cause modifications to occur in the colour of the material.
  2. Aided in quantifying the discolouration for both processes and from this experiment it was evidently shown that gamma irradiation was the most detrimental method of the two.

Polypropylene (PP)

Samples Preparation

Material

PP material which is an impact polymer grade (PP7043L1) manufactured by ExxonMobil Chemical Company .

- Melt flow index (MFI): 8.0g/10min under loading of 2.16kg at 230°C,
- Density: 0.9g/cm^3
- Impact strength: 13kJ/m2 at 23°C
- Melt temperature: 161°C.

Injection moulding and packaging

An Arburg injection moulding machine was utilised in manufacturing type IV ASTM D638 testing specimens.

Sample preparation played a significant role in the radiation process as this controlled the uniformity of the irradiation dose on the samples.

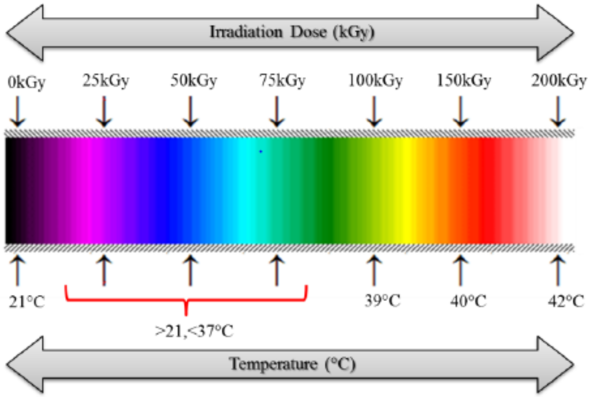
Thermax® irreversible temperature labels ranging were placed on the samples during irradiation so as to identify the maximum temperature achieved during the process.

Polypropylene (PP) – Cont.

Samples Irradiation

Electron beam irradiation

Accelerator Type: Mevex high energy electron beam Linac Accelerator (10MeV unit, 20KW)
Irradiation Doses: 25, 50, 75, 100, 150 and 200kGy.
Dose rate: approx. 12.5kGy per pass on each side.
Irradiation Conditions: Room temperature in the presence of air (max. temperature reached was approx. 42°C on the 200kGy samples.)
Note that non-irradiated samples served as the baseline for each of the test.



Gamma ray irradiation

Accelerator Type: A gamma irradiator using a cobalt 60 energy source (circa 3.5 MCi)
Irradiation Doses: 25 and 200kGy
Dose rate: approx. 8 kGy per hour.
Irradiation Conditions: Room temperature in the presence of air .
Note that non-irradiated samples served as the baseline for each of the test.

Polypropylene (PP) – Cont.

<u>Characterisation Tests Completed</u>

- **Melt flow index (MFI):**
  The melt flow index (MFI) is a measure of the ease of flow of the melt of a thermoplastic polymer.

- ***Fourier transform infrared spectroscopy (FTIR).***
  This is a measurement technique that allows one to record infrared spectra and identify differences in different group of one or more molecules..

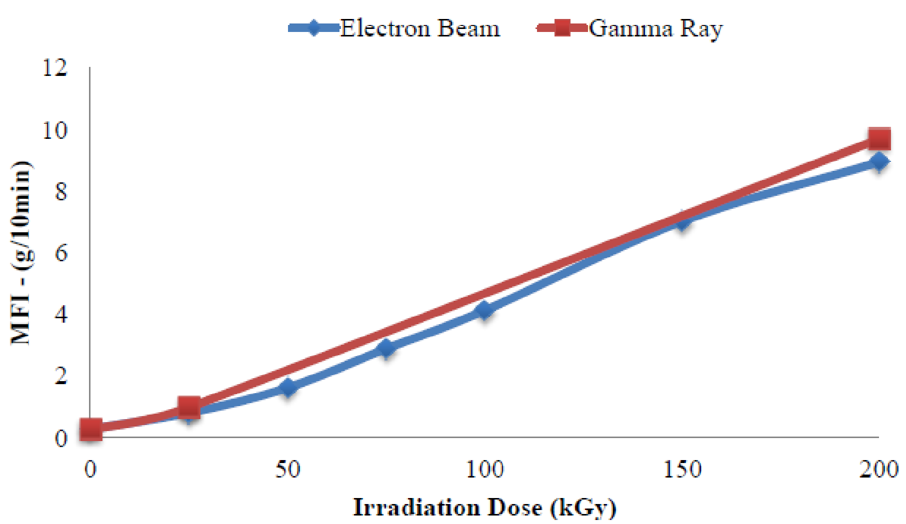
- *Dynamic Frequency Sweeps (***Rheology Study***):* A frequency sweep is a test that enables the viscoelastic properties of a sample to be determined as a function of timescale.

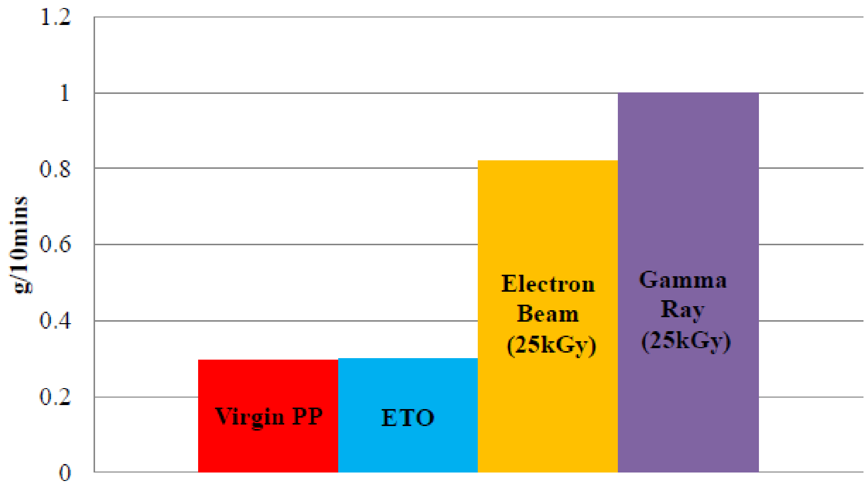
- *Colorimetry* .

Polypropylene (PP) – Cont.

Characterisation Tests Results

- ***Melt flow index (MFI).***
  The MFI experiment illustrated a dramatic reduction in the melting strength and molecular weight of the PP material as a result of radiation induced free radical reaction. However, the gamma irradiated samples had slightly higher MFI values to that of the electron beam irradiated samples. This suggested that the gamma ray process triggered more degradation effects upon irradiation exposure.





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Polypropylene (PP) – Cont.

Characterisation Tests Results

- *Fourier transform infrared spectroscopy (FTIR).*
  These test results confirmed that oxidation and scission is taking place proportional to radiation. The effect is slightly greater for the gamma radiation process in comparison to the E-Beam process.

Table 1, Main peak heights obtained for the non-irradiated and irradiated (electron beam and gamma ray) PP material

Irradiation Dose (kGy)	Irradiation Process	Wave No. (cm-1)							
		1457 cm-1	1376 cm-1	1166 cm-1	1000 cm-1	973 cm-1	840 cm-1	810 cm-1	720 cm-1
0	Baseline Sample	82.70	74.61	95.23	95.26	93.10	94.89	96.73	97.72
25	Electron Beam	81.44	72.25	94.96	94.90	92.59	94.44	96.47	97.68
200	Electron Beam	76.95	66.36	92.16	92.90	90.68	92.83	95.00	96.19
25	Gamma Ray	77.01	66.20	93.28	93.42	90.66	93.17	95.75	97.33
200	Gamma Ray	78.35	64.40	91.08	91.86	90.11	91.35	93.54	95.32

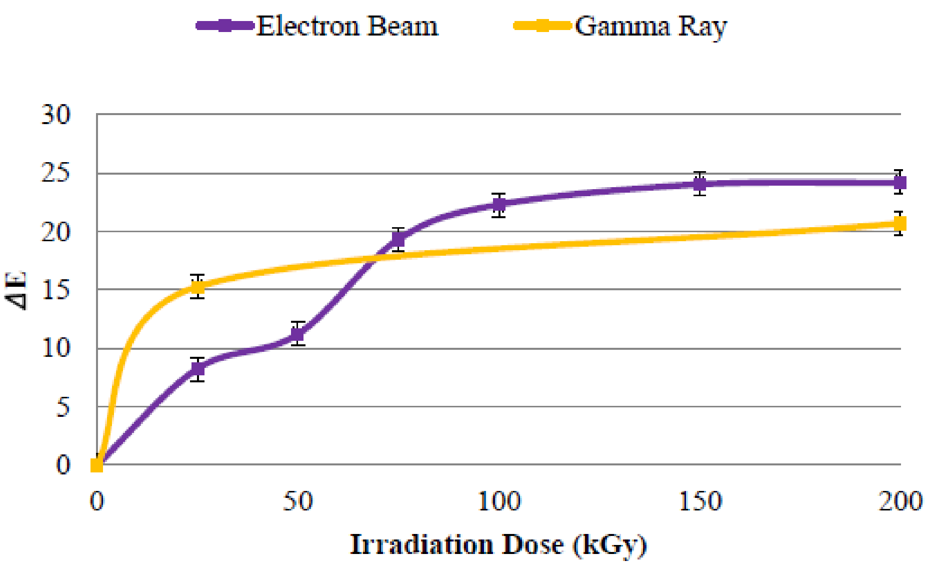
methyl group

Polypropylene (PP) – Cont.

Characterisation Tests Results

- *Dynamic Frequency Sweeps*
  Dynamic frequency sweep tests performed by the rheology machine emphasised the changes to polymer structure which arose after irradiation exposure. It was apparent that the gamma ray process was causing more alterations to transpire in the material. This was a result of scissioning of the polymeric chains caused by the formation of free radicals.

- *Colorimetry*
  Both the electron beam and gamma ray processes cause modifications to occur in the colour of the material.
  While the change is greater for gamma irradiation between 0 and 50kGy, the tendency is inverted above 50kGy.



Poly (ether-block-amide) thermoplastic elastomers (PEBA)

Samples Preparation

Material

PEBAX 6333 SA01 is a medical grade poly(etherblockamide) virgin polymer manufactured by Arkema.

- Density: 1.01g/cm3
- Melt temperature: 169.1°C.

Injection moulding and packaging

An Arburg injection moulding machine was utilised in manufacturing type IV ASTM D638 testing specimens.

Sample preparation played a significant role in the radiation process as this controlled the uniformity of the irradiation dose on the samples.

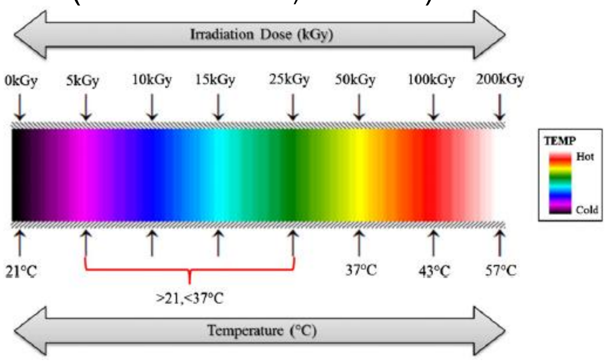
Thermax® irreversible temperature labels ranging were placed on the samples during irradiation so as to identify the maximum temperature achieved during the process.

Poly (ether-block-amide) thermoplastic elastomers (PEBA) – Cont.

Samples Irradiation

Electron beam irradiation

Accelerator Type: Mevex high energy electron beam Linac Accelerator (10MeV unit, 20KW)
Irradiation Doses: 5,10,15,25,50, 100 and 200 kGy.
Dose rate: approx. 12.5kGy per pass on each side.
Irradiation Conditions: Room temperature in the presence of air (max. temperature reached was approx. 57°C on the 200kGy samples.)
Note that non-irradiated samples served as the baseline for each of the test.



Gamma ray irradiation

Accelerator Type: A gamma irradiator using a cobalt 60 energy source (circa 3.5 MCi)
Irradiation Doses: 25 and 200kGy.
Dose rate: approx. 8 kGy per hour.
Irradiation Conditions: Room temperature in the presence of air
Note that non-irradiated samples served as the baseline for each of the test.

Poly (ether-block-amide) thermoplastic elastomers (PEBA) – Cont.

Characterisation Tests Completed

- **Tensile testing:** Properties that are directly measured via a tensile test are ultimate tensile strenght and maximum elongation.
- *Shore D hardness*
- *Melt flow index*
- *Attenuated total reflectance Fourier transform infrared spectroscopy*
- *Colorimetry* .

Poly (ether-block-amide) thermoplastic elastomers (PEBA) – Cont.

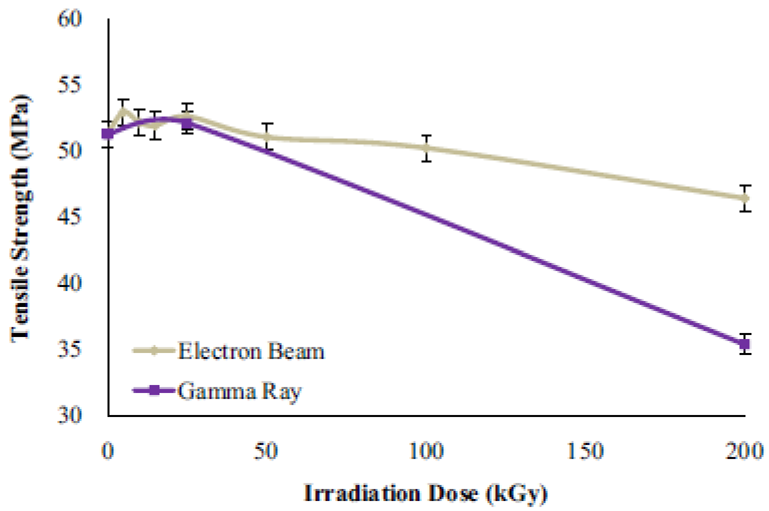
Characterisation Tests Results

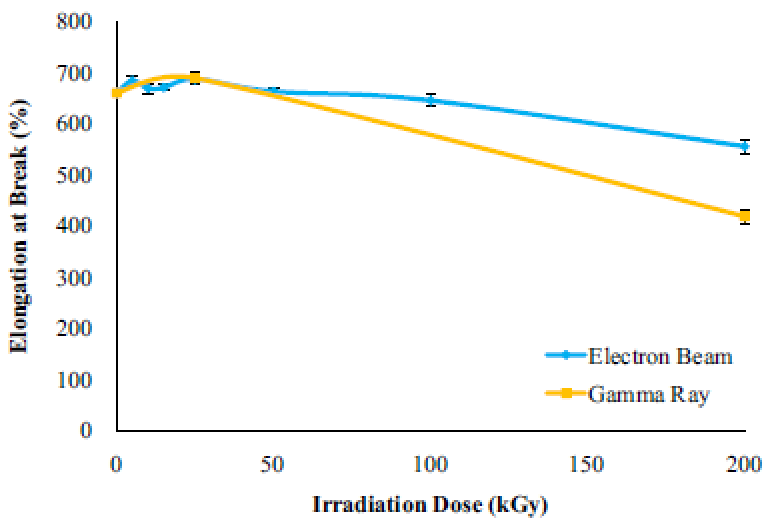
- *Tensile test*

  Both the electron beam and gamma ray processes show an increase in tensile strength between 0 and 25kGy with E-Beam processed samples being the most affected between 0 and 25kGy, the tendency is inverted above 25kGy, the tensile strength decreased.

  Potential caused: This could be due to branching and chain scissioning occurring simultaneously. Branching can limit the packing of polymer chains and lead to the formation of free volume in the material, hence causing a reduction in the tensile strength. This effect is more serve with gamma irradiation process.

  The result of the elongation at break confirms this theory.



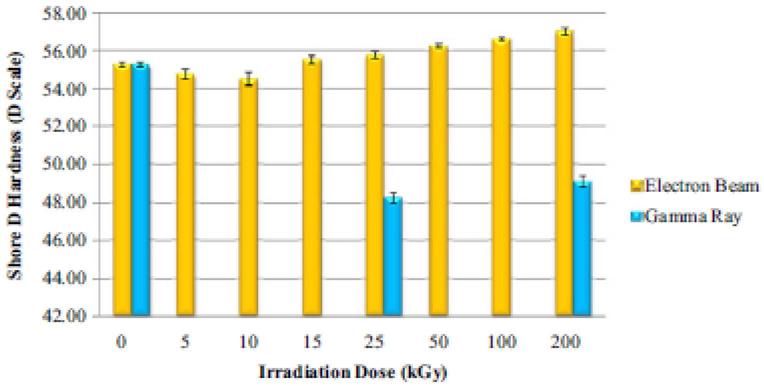


Poly (ether-block-amide) thermoplastic elastomers (PEBA) – Cont.

Characterisation Tests Results

- ***Shore D hardness***

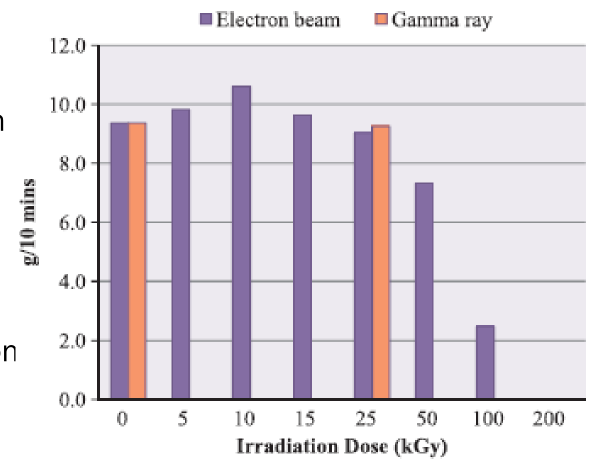
  The hardness of PEBA increase slightly as dose increase for E-Beam irradiation process, as expected, but not significantly. Changes to the hardness was more obvious after gamma irradiation; these changes were possibly related to the breaking down of molecular chains on account of radiation degradation.



- ***Melt Flow Index***

  For electron beam samples, an increase in the MFI value was observed between 0 and 10kGy. Above this dose, the MFI value started to reduce considerably, it is an indication that the molecular weight decreased at the low dose rates which can be attributed to degradation (chain scission). From 10kGy, the MFI value decreased dramatically signifying that the molecular weight increased leading to a restriction in the flow properties. Gamma irradiated samples show similar results as E-Beam at 25kGy and 200kGy.

  Overall, it could be suggested that the predominant phenomenon throughout this experiment has been crosslinking, due to the notable reductions in the MFI values for both processes.



Irradiation Dose (kGy)	Standard Error (Electron Beam Samples)	Standard Error (Gamma Ray Samples)
0	0.01	0.01
5	0.01	-
10	0.03	-
15	0.01	-
25	0.01	0.00
50	0.00	-
100	0.01	-
200	0.00	0.00

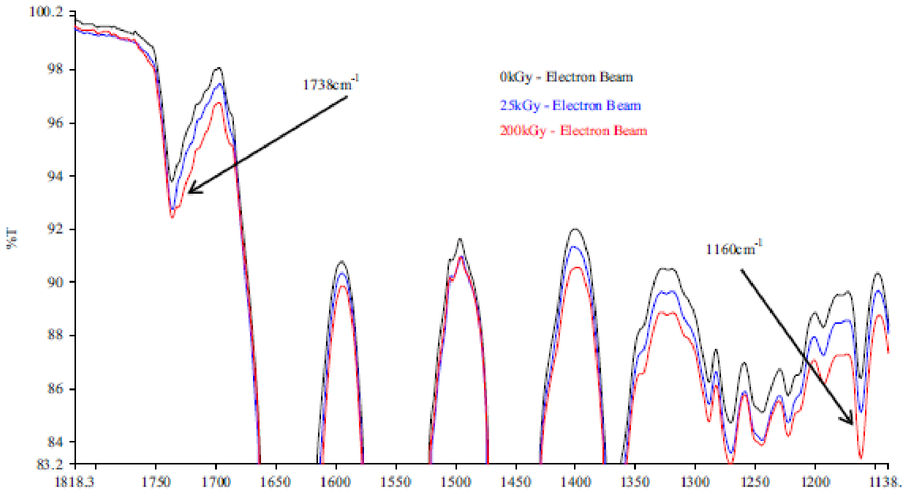
Poly (ether-block-amide) thermoplastic elastomers (PEBA) – Cont.

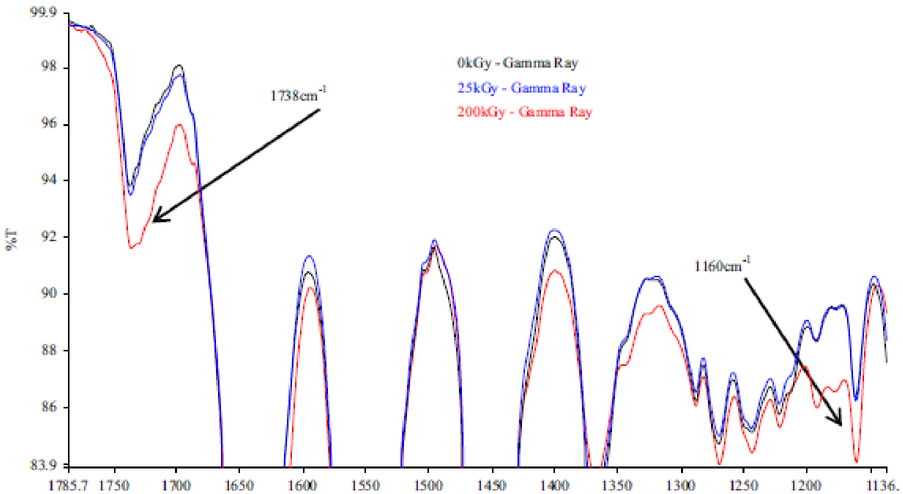
Characterisation Tests Results

- *Attenuated total reflectance Fourier transform infrared spectroscopy*

<u>*Peak at 1160 cm^{-1}*</u>: The increase of this peak for both irradiation processes signifies that the polyether segment of the copolymer is branching as the dose increase.
At 25kGy. the branching is more significant for E-Beam than Gamma; however, this opposite applies at 200kGy dose level.

<u>*Peak at 1738 cm^{-1}*</u>: This is a representation of the vibrational stretching of the ester carbonyl functional group in the material
At the lower dose of 25kGy, electron beam irradiated samples demonstrated more oxidative products in contrast to gamma irradiated samples. However, at the higher dose rate of 200kGy, gamma irradiation demonstrated to be the more detrimental irradiation process.





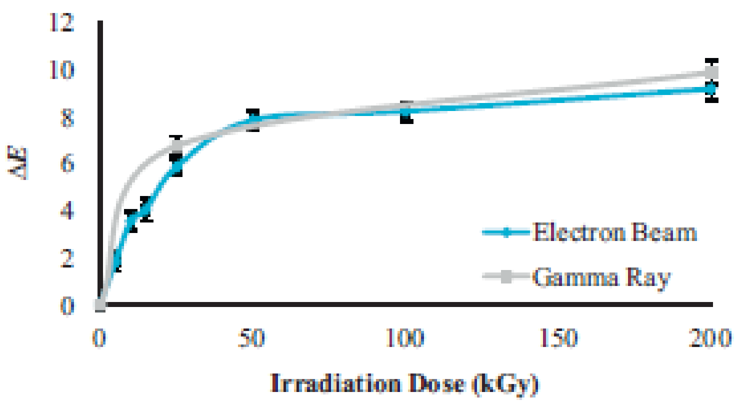
Poly (ether-block-amide) thermoplastic elastomers (PEBA) – Cont.

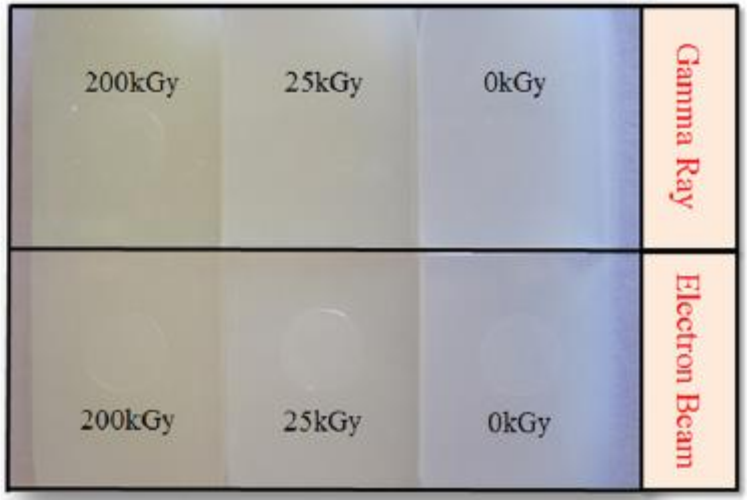
Characterisation Tests Results

- *Colorimetry*

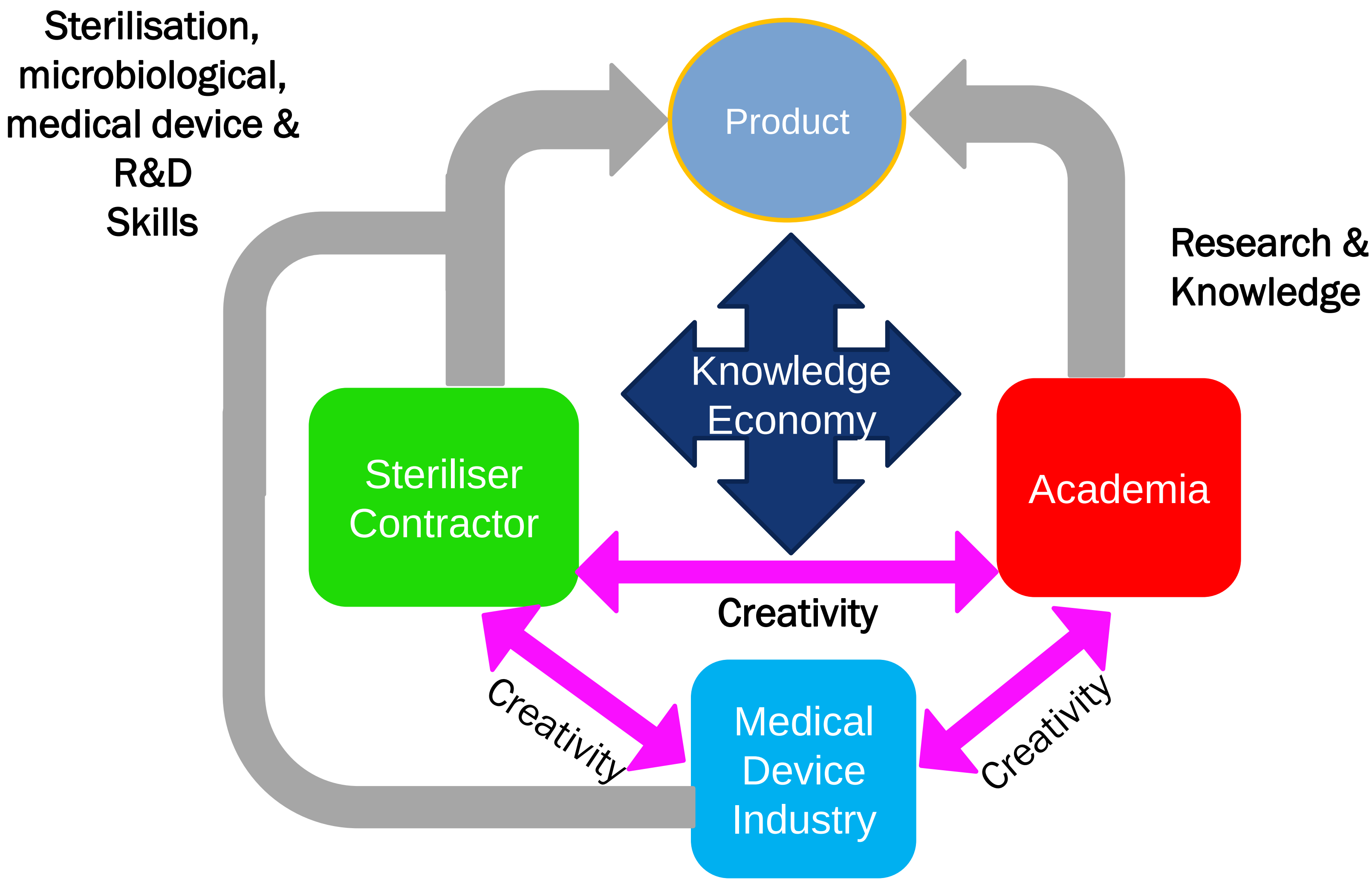
  The graph below shows that gamma ray process lead to more discolouration in the PEBA material throughout all irradiation dose ranges implemented.

  Potential caused: Such alterations could be attributed to oxidation which may have arisen from the irradiation processing in an air atmosphere. Discoloration can result from the formation of conjugated double bonds in polymers during the irradiation process.





Where do we go from here?



Reference Publications

Characterisation of the Surface and Structural Properties of Gamma Ray and Electron Beam Irradiated Low Density Polyethylene

Kieran A. Murray, James E. Kennedy, Brian McEvoy, Olivier Vrain, Damien Ryan, Richard Cowman, Clement L. Higginbotham

From the International Journal of Material Science (IJMSCI) Volume 3 Issue 1, March 2013

Effects of gamma ray and electron beam irradiation on the mechanical, thermal, structural and physicochemical properties of poly (ether-block-amide) thermoplastic elastomers

Kieran A. Murray, James E. Kennedy, Brian McEvoy, Olivier Vrain, Damien Ryan, Richard Cowman, Clement L. Higginbotham

From the journal of the mechanical behavior of biomedical materials 17 (2013) 252–268

Comparative study on the degradation effects initiated by gamma ray and electron beam irradiation in polypropylene

Kieran A. Murray, James E. Kennedy, Brian McEvoy, Olivier Vrain, Damien Ryan, Richard Cowman, Clement L. Higginbotham

Thank-you for listening. Any questions?