NEW OPPORTUNITIES FOR THE UTILIZATION OF ELECTRON ACCELERATORS IN POLYMER PROCESSING INDUSTRIES

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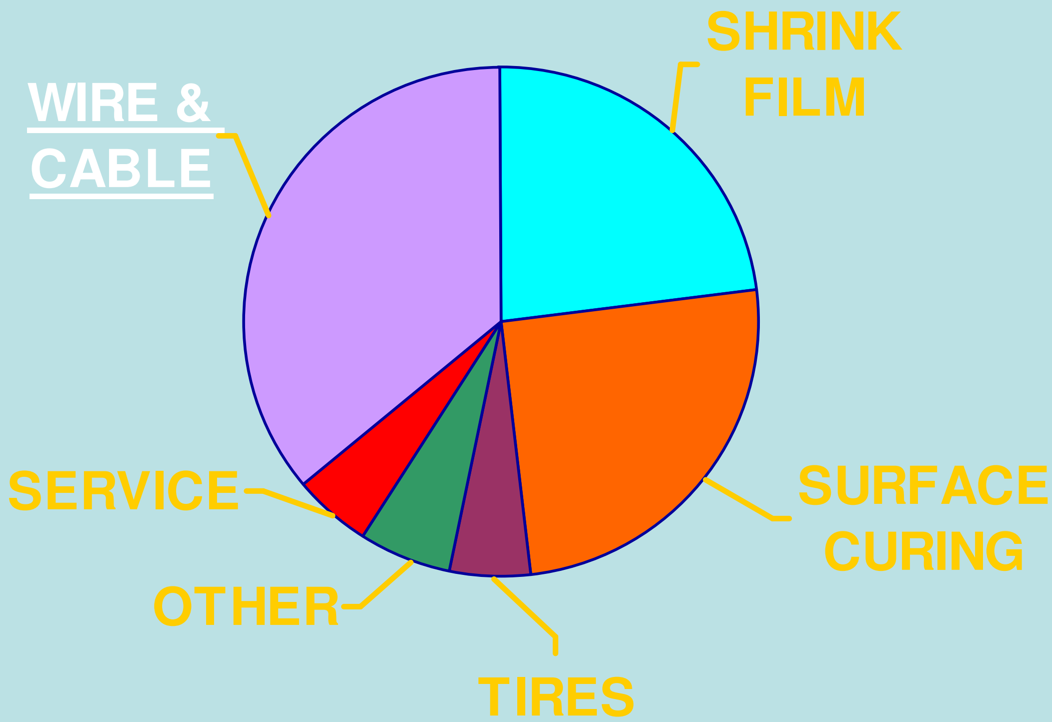
INDUSTRIAL RADIATION TECHNOLOGY

- **Health-care Applications**
- **Polymer Processing**
- **Environmental Applications**
- **Food Irradiation**

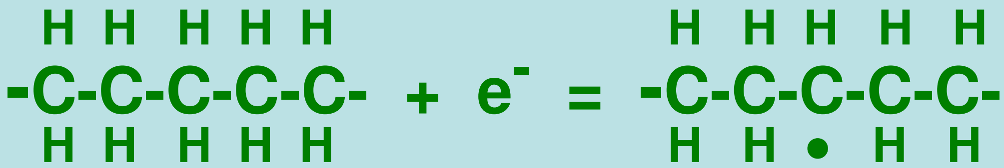
Established Applications in Polymer Processing

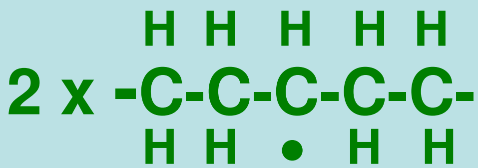
- Wire and Cable
- Tubing
- Heat-shrinkables
- Surface Curing
- Tyres
- Teflon

Electron Beam Market

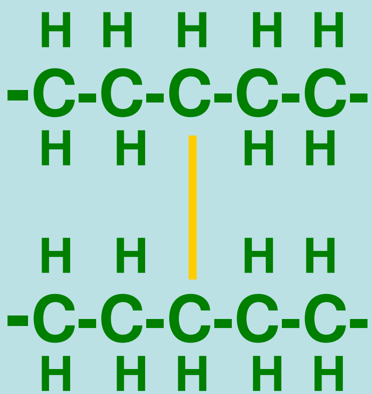


Crosslinking of Polyethylene





Hydrogen Abstracted



Radicals Combine

Crosslinked PE

Emerging Applications in Polymer Processing

- Crosslinking
- Curing
- Grafting
- Chain Scissioning

Crosslinking

- Any Physical State and Shape
- Any Temperature
- No Additives
- High Throughput

Crosslinking

- Teflon
- UHMWPE
- Polycarbonate
- Polyamide
- Poly(butylene terephtalate)
- Hydrogels
- RVNRL

PTFE cross-linked by radiation

PTFE : ~ CF2 - CF2 - CF2 ~

Mp: 327℃

Crosslinking condition

Temperature: 330 - 340℃

Atmosphere: Inert gas

Properties of cross-linked PTFE

Transparency by low crystallinity

Radiation resist: 2 order improved

Wear resist: 3 order improved

Electric resistance: not changed

Chemical resistance: not changed

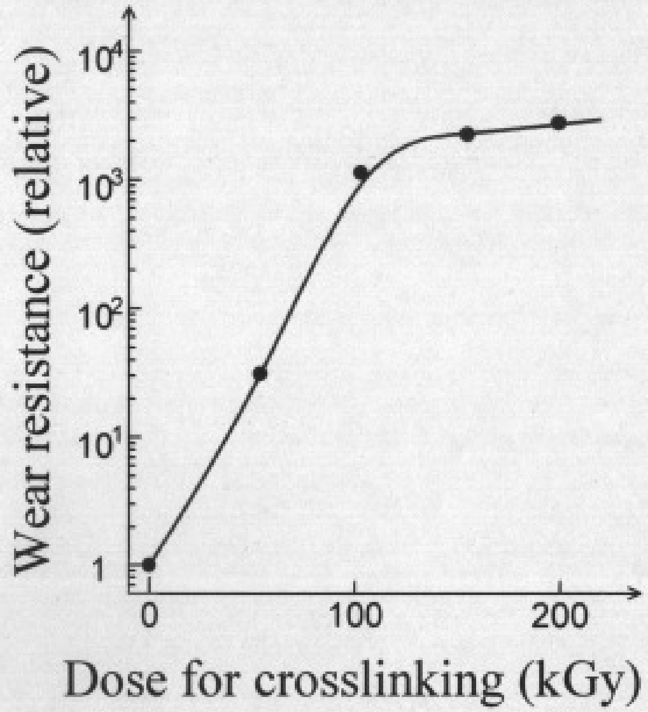
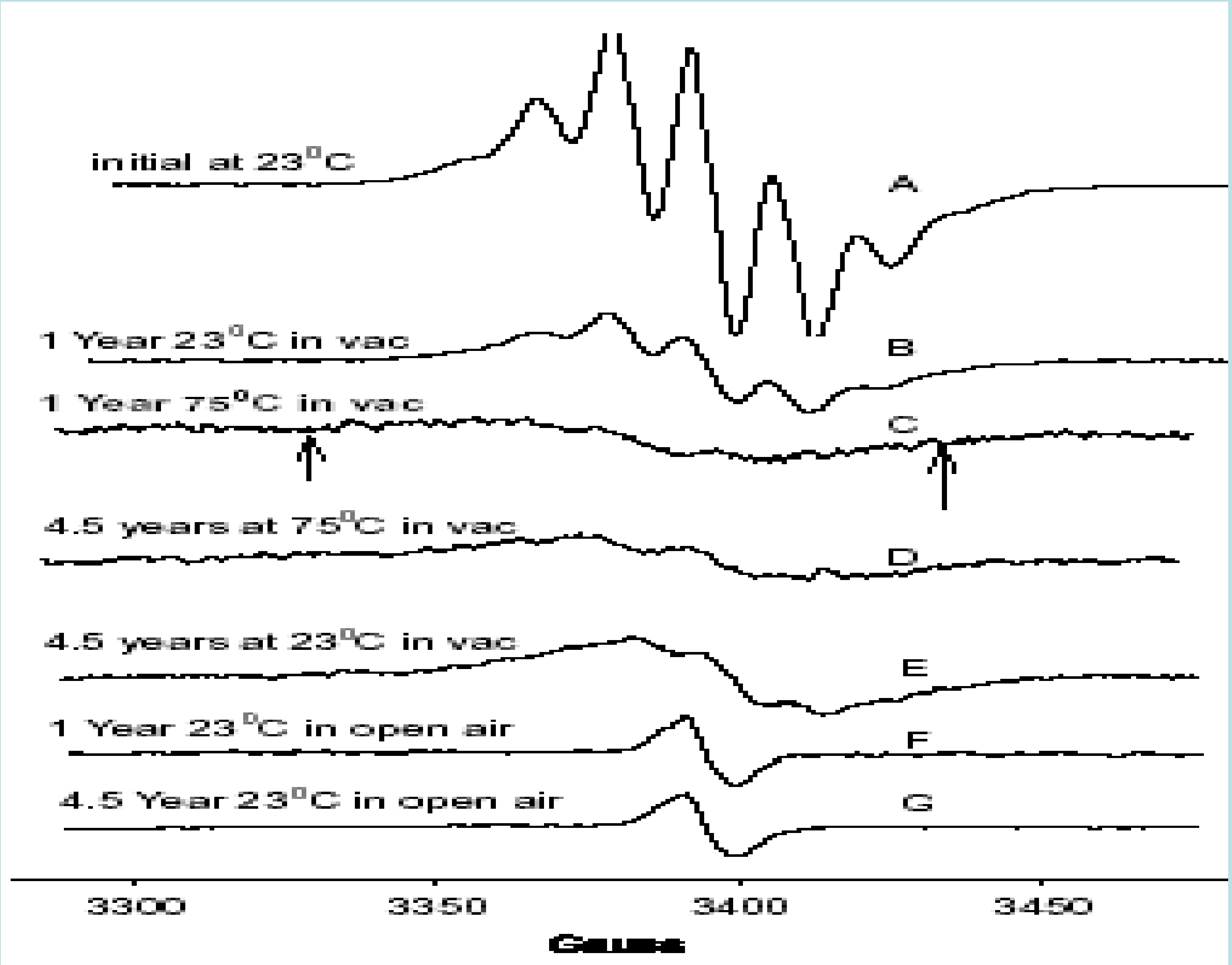


Fig. 2. Delamination associated with oxidation of: (a) UHMWPE tibial knee component and (b) UHMWPE acebatular hip component.

Trapped Radicals in Gamma-irradiated UHMWPE



Aging of UHMWPE tibilar knee

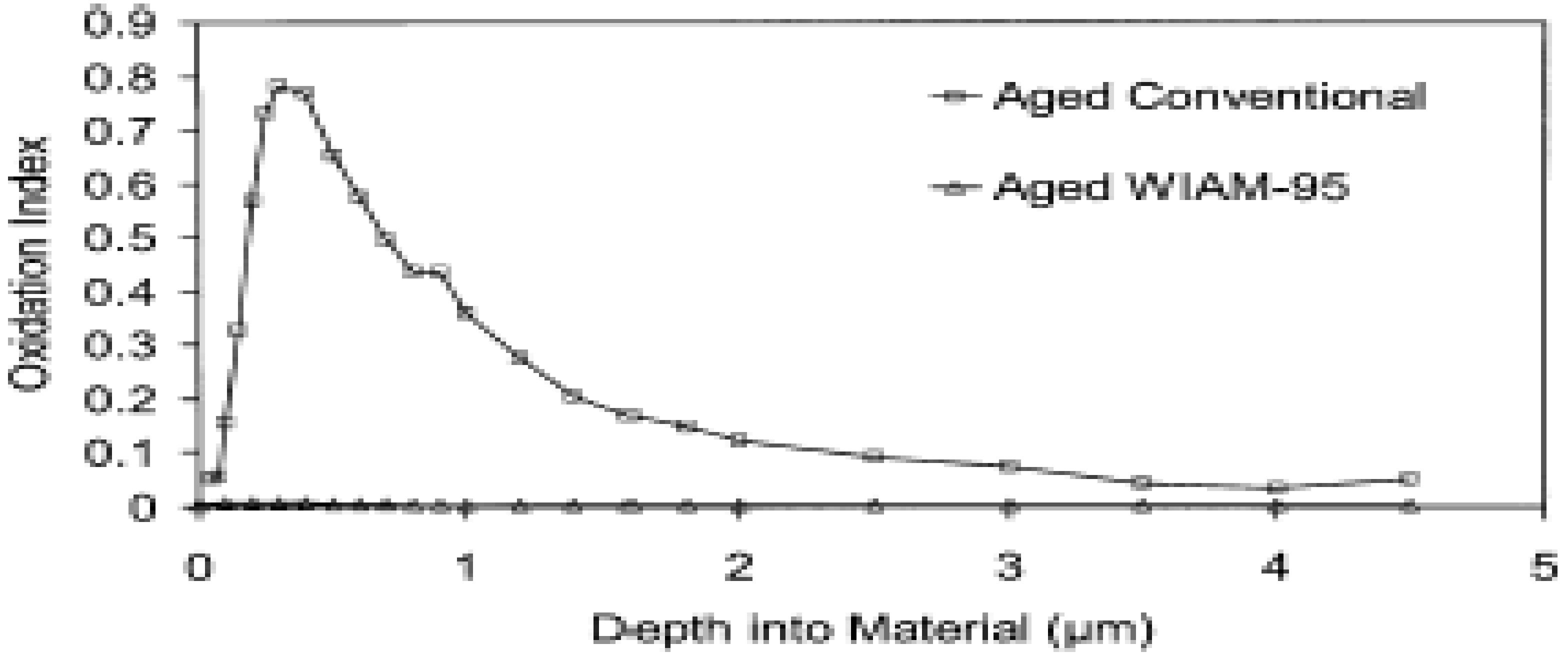


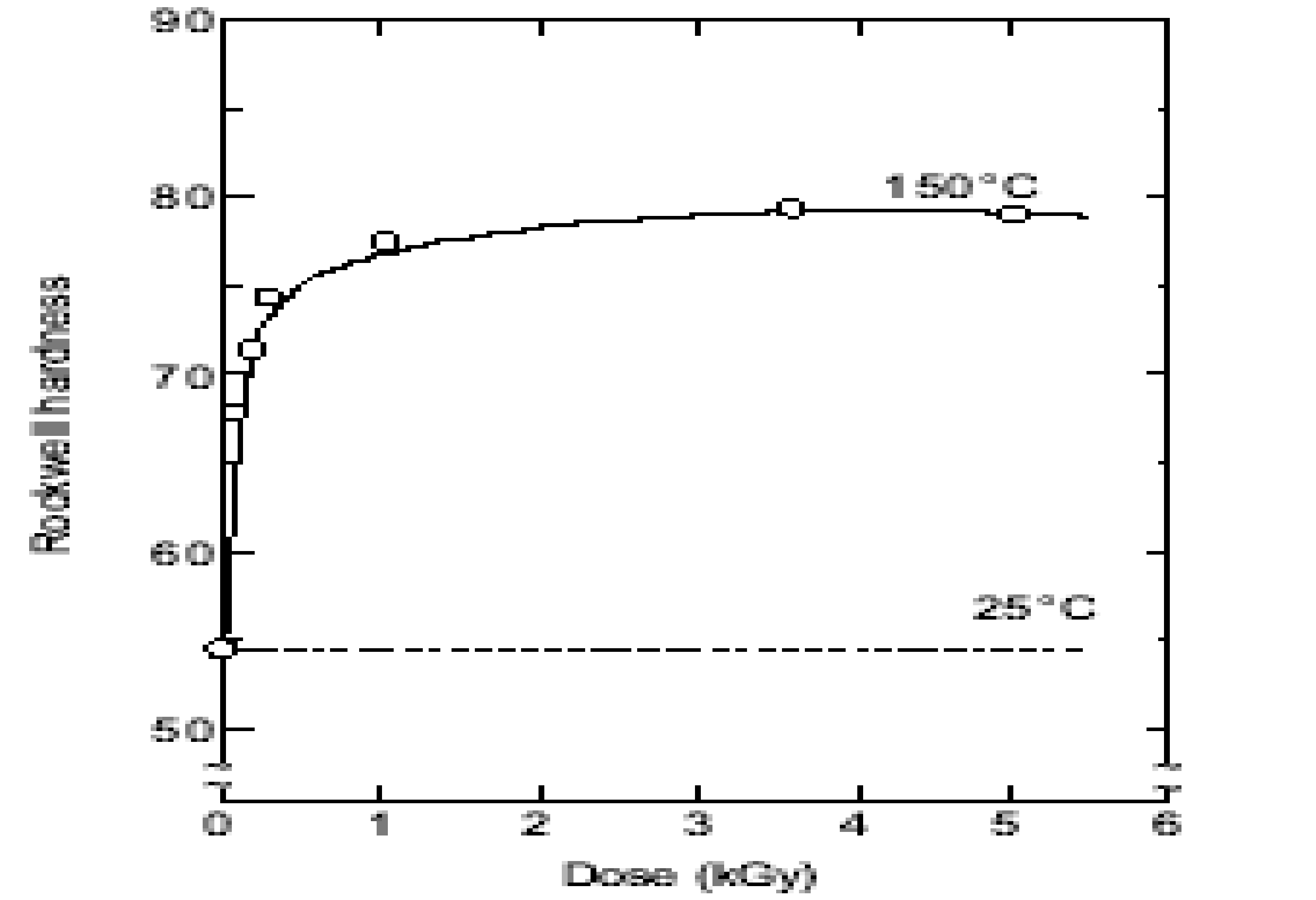
Fig. 5. Representative oxidation index values measured as a function of depth away from the articulating surface of the conventional and highly cross-linked polyethylene tibial knee inserts following the 35 days of accelerated aging at 80°C in air.

Current applications of highly crosslinked polyethylenes in total hip replacements.

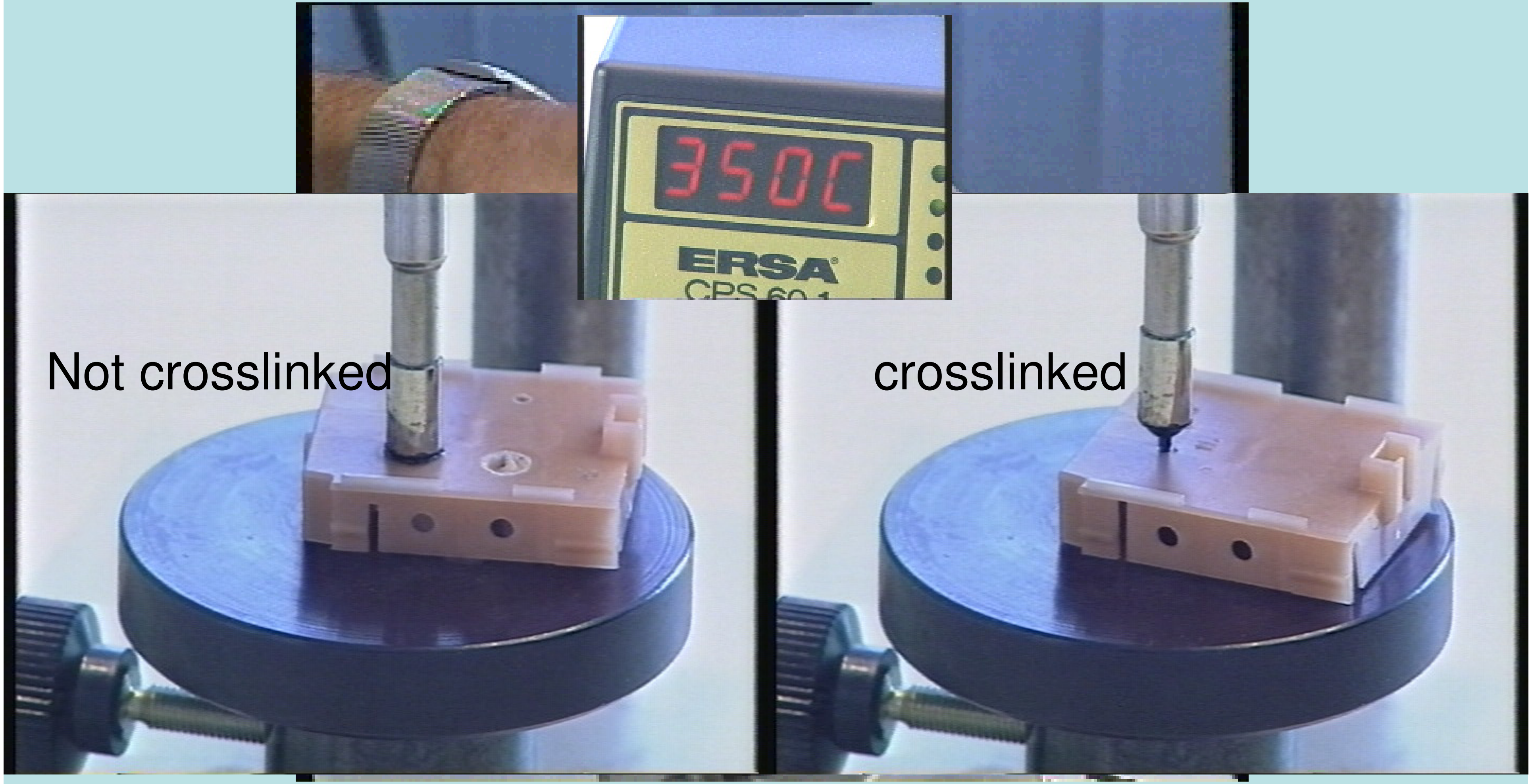
	Manufacturer	*Radiation Temperature*	*Radiation Dose (kGy*)*	*Radiation Type*	*Post-irradiation Thermal Treatment*	*Sterilization Method*	*Total Radiation Dose Level (kGy)*	*Residual free radicals present?*
Longevity™	Zimmer	~40°C	100	E-beam	Melted at 150°C for 6 hours	Gas Plasma	100	No
Durasul™	Sulzer	~125°C	95		Melted at 150°C for 2 hours	EtO	95	No
Marathon™	Depuy/JJ	RT	50	Gamma	Melted at 155°C for 24 hours	Gas Plasma	50	No
XLPE™	Smith & Nephew	RT	100		Melted at 150°C for a proprietary duration	EtO	100	No
Crossfire™	Stryker/Osteonics/Howmedica	RT	75		Anneal at 120°C for a proprietary duration	Gamma (30 kGy) in nitrogen	105	Yes
Aeonian™	Kyocera	RT	35		Annealed at 110°C for 10 hours	Gamma (25-40 kGy) in nitrogen	60-75	Yes

* 10 kilogray (kGy) = 1 megarad (Mrad)
RT = Room Temperature

Irradiated Polycarbonate



Measurement of the heat resistance with a soldering iron



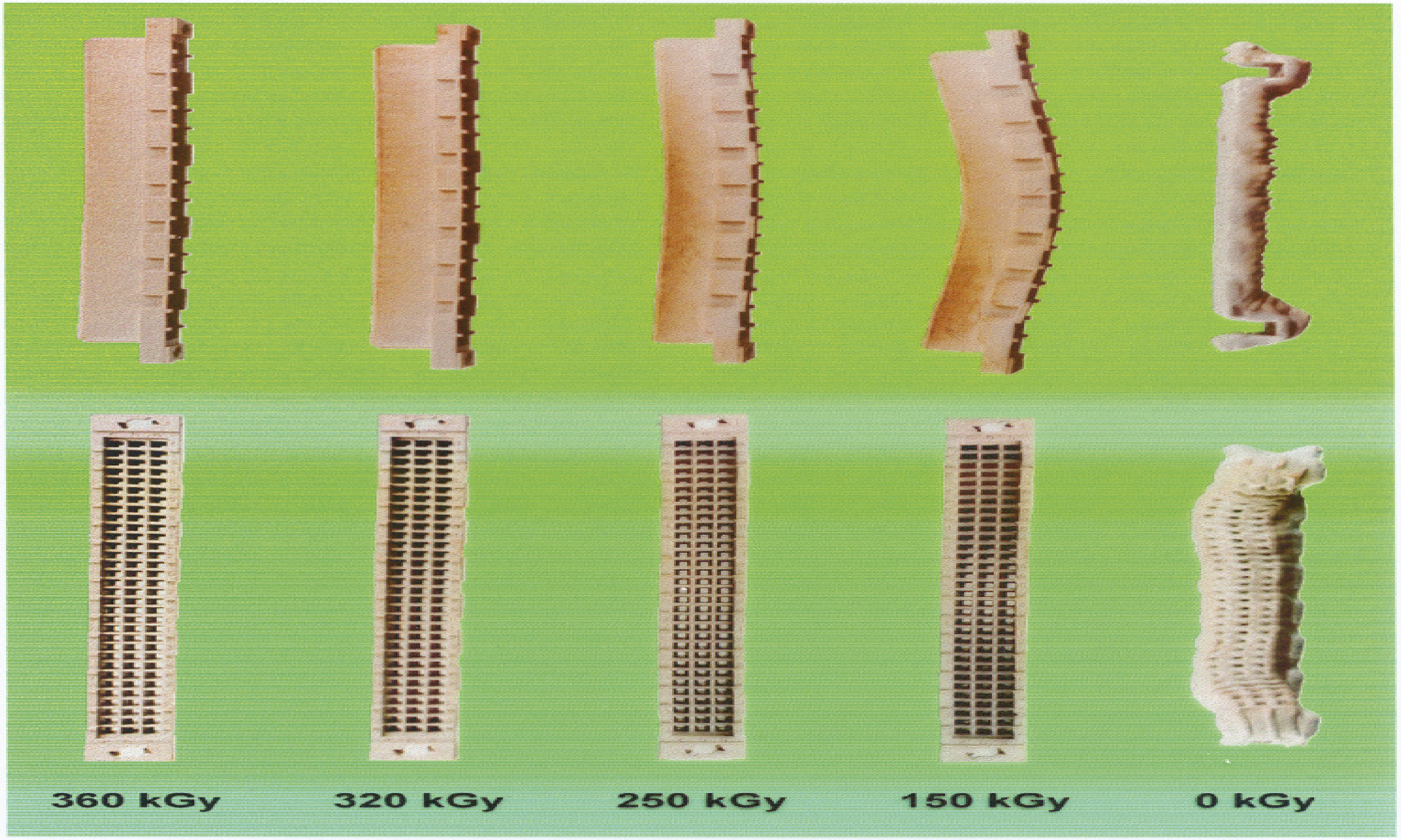
Material: PA 6 GF30 **Weight: 1000g** **Temperature: 350°C** **BGS**

BETA-GAMMA-SERVICE

Degussa-Hüls
Engineering Plastics

Results of the temperature test of connectors out of VESTODUR® X9410

300 °C
12 min



Test procedure: connectors are crosslinked with different energies and stored in an oven with a constant temperature of **300°C** up to **12 minutes**. The connectors are based on abutment with a distance of 70 mm without a mechanical load.

Hydrogel Wound Dressing

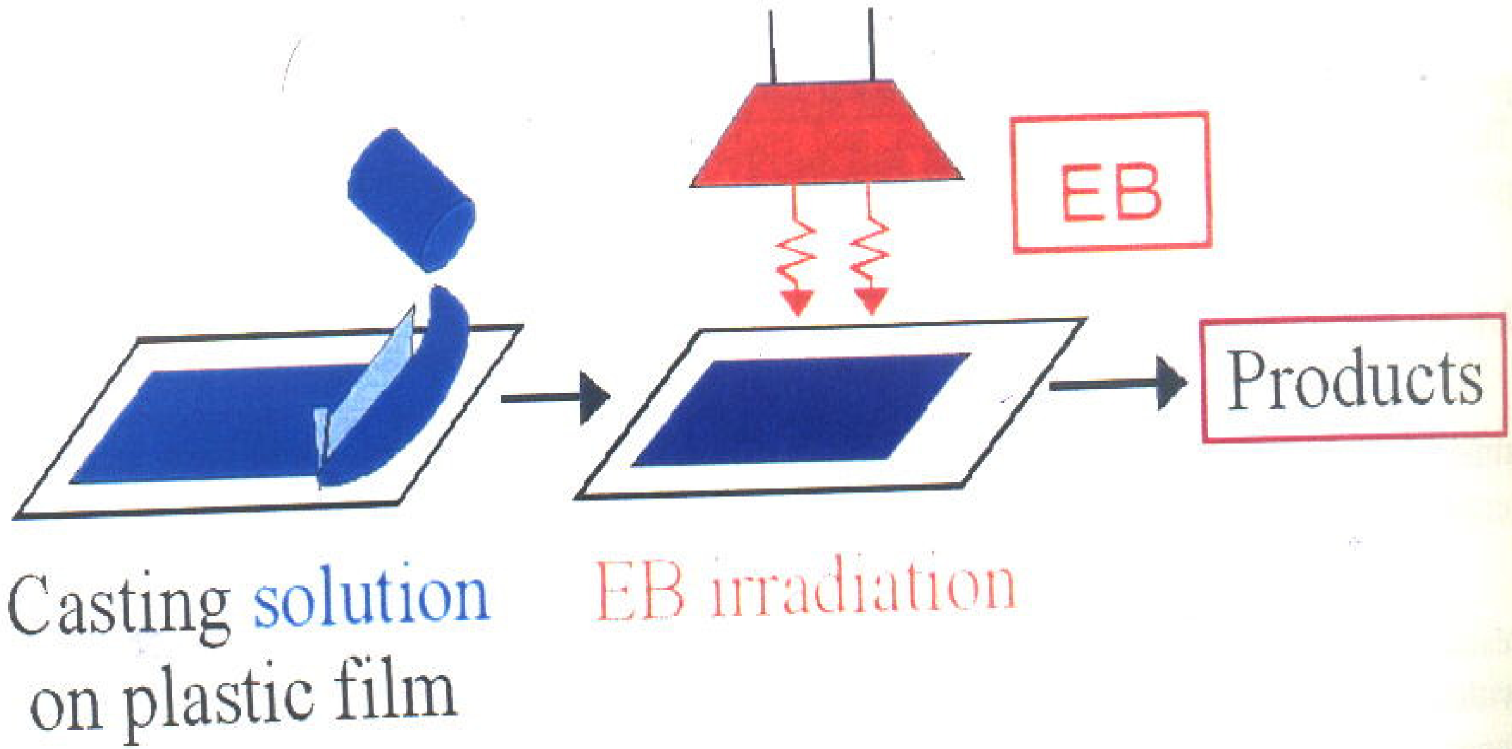
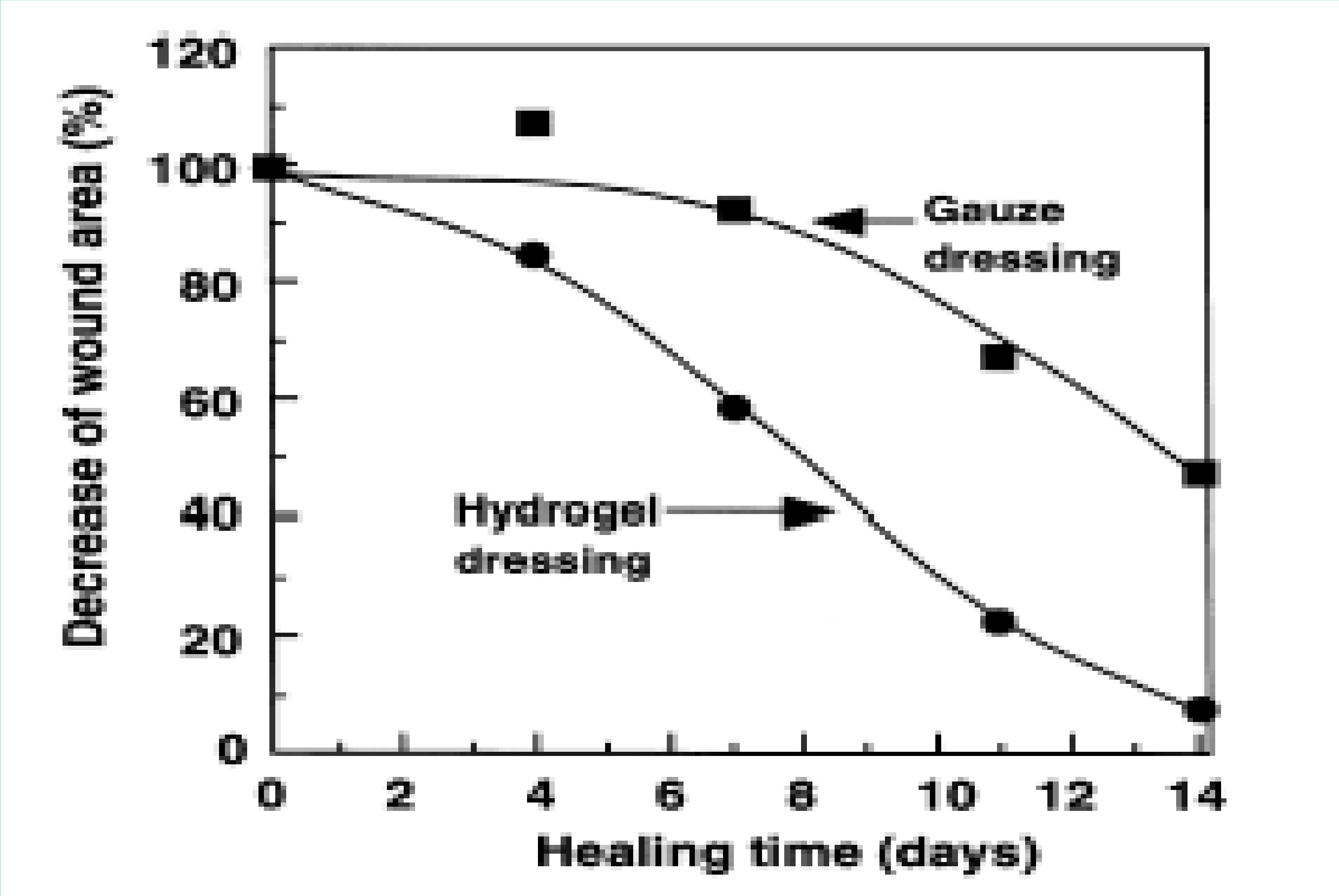
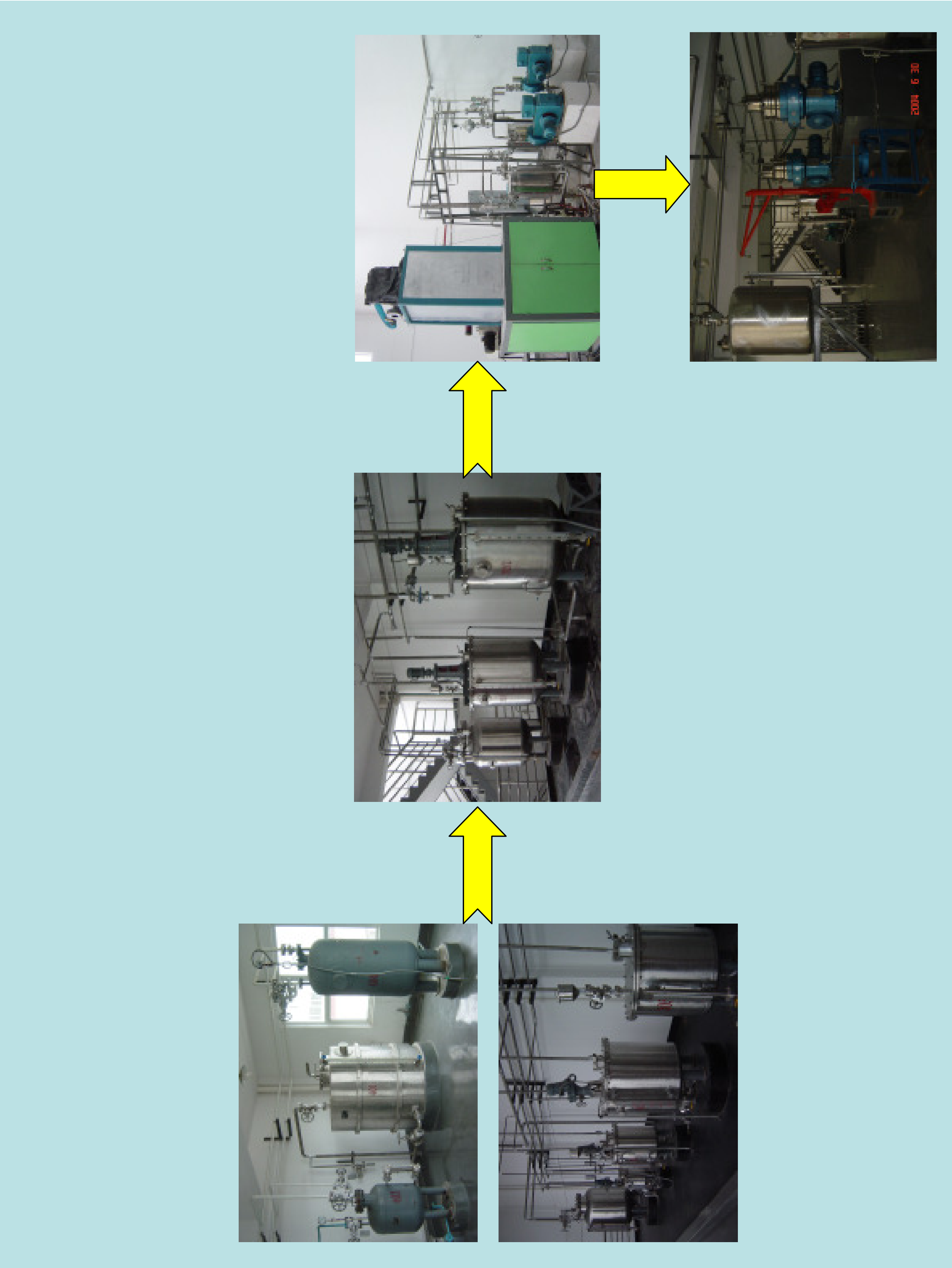


FIG. 2. EB Process for Hydrogel Wound Dressing

Hydrogel Wound Dressing

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Curing

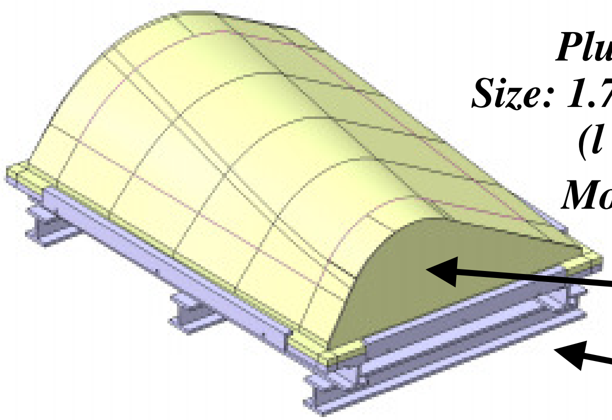
Solvent-free, Energy savings, High extent of cure, High throughput

- **Composites**
- **Nanocomposites**

Low Cost Fairings Project: Results

Step 1) Select a complex aerospace part shape. Obtain a plug with this shape to act as the mould for producing the EB tool.

Part selected, Plug materials optimal for EB curing were determined. A plug containing these materials was purchased from a commercial source.

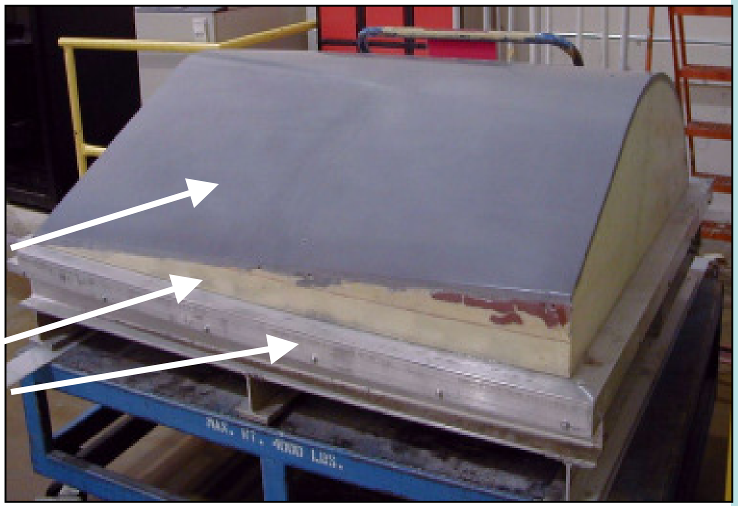


Plug Weight: 400 kg
Size: 1.7 m x 1.2m x 0.7 m (l x w x h)

Modeling Paste Surface

Low density Foam

Aluminum I-Beam Frames (2)

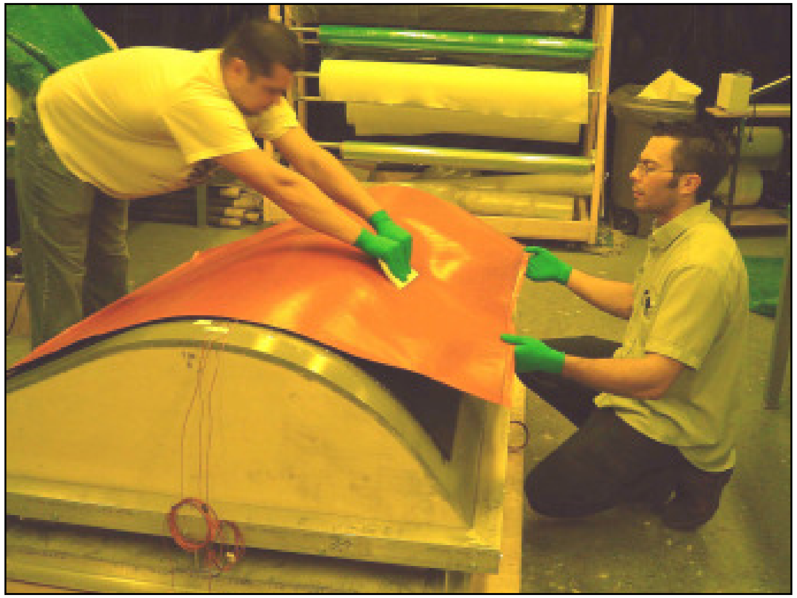


Low Cost Fairings Project: Results

Step 2) Manufacture a tool on the plug for producing composite parts .

a) Fabrication of tool surface on the plug using EB curing

Composite ply lay-up on plug



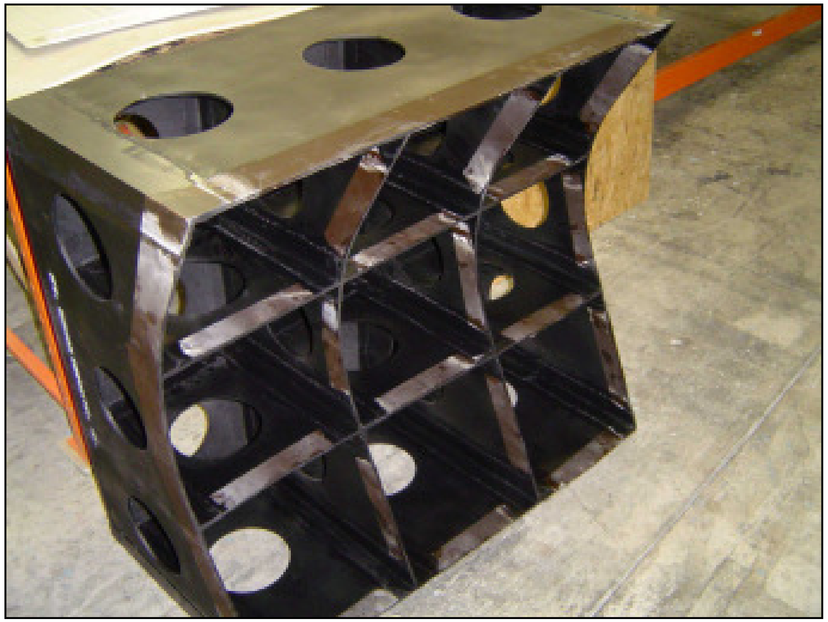
Positioning on Conveyor for EB Curing

Low Cost Fairings Project: Results

Step 2) Manufacture a tool for producing composite parts

b) Application of Egg Crating to Stabilize Shape

Egg Crating Structure

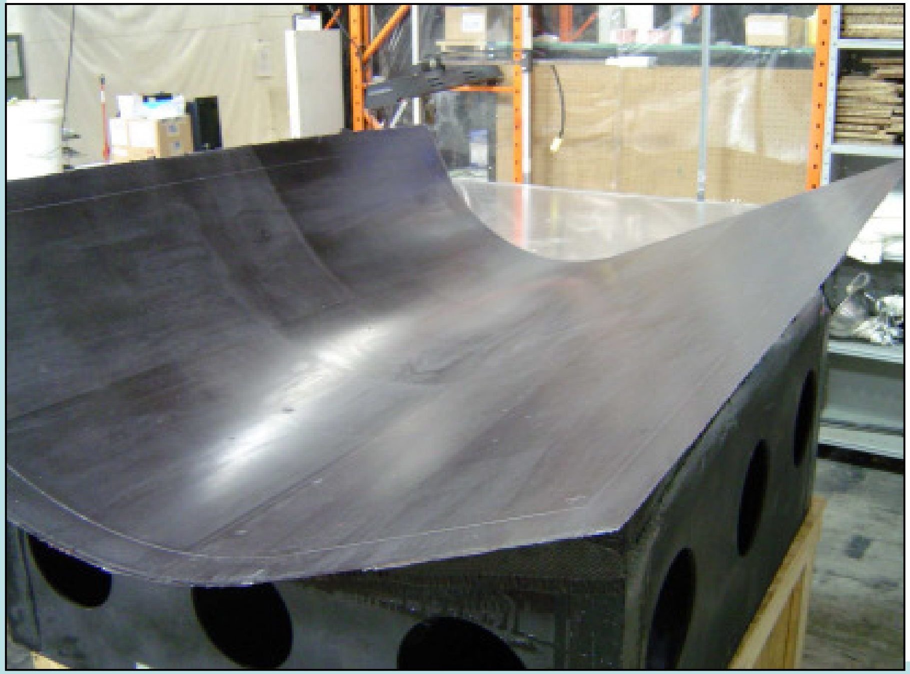


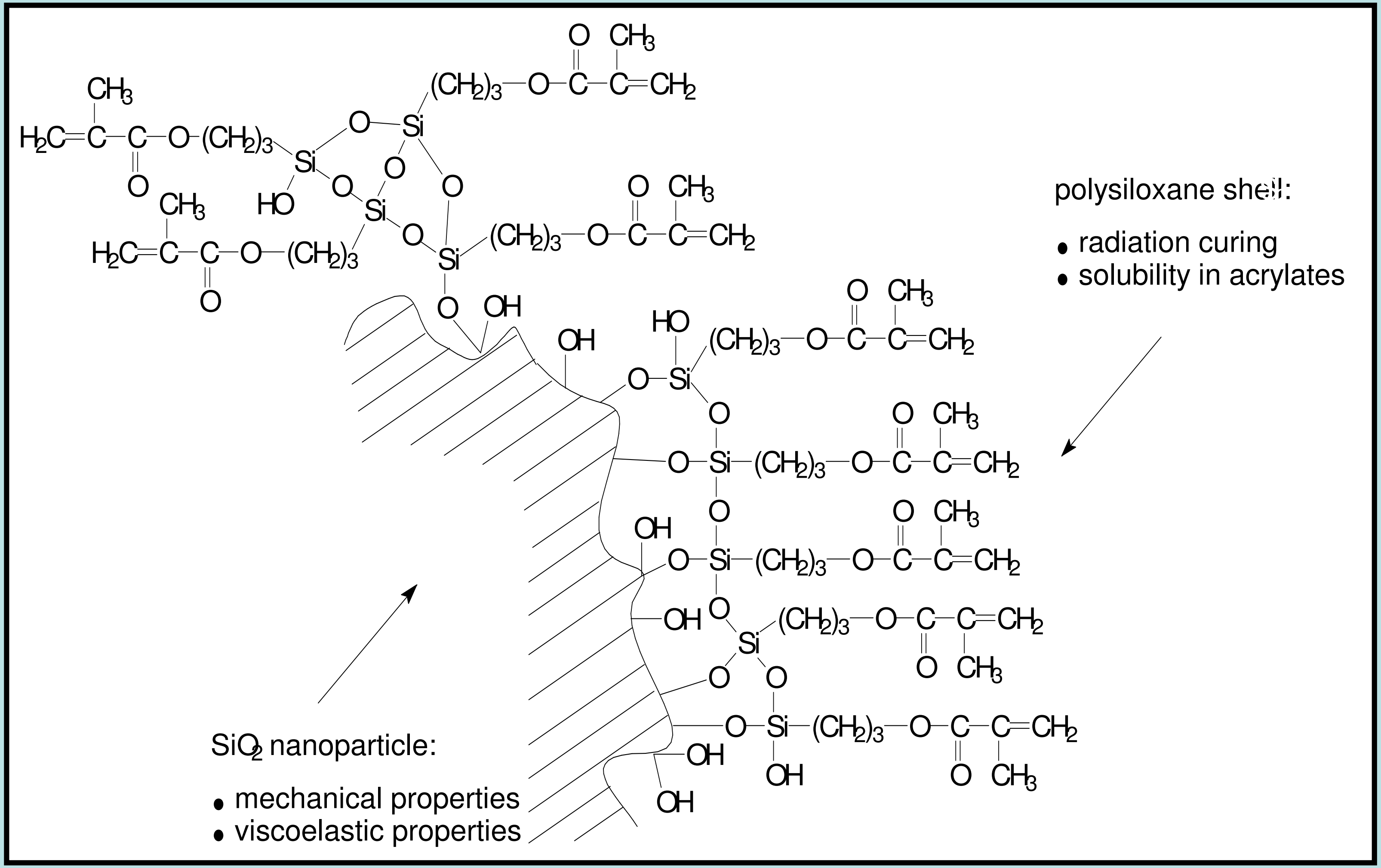
Application on EB Cured Tool

Low Cost Fairings Project: Results

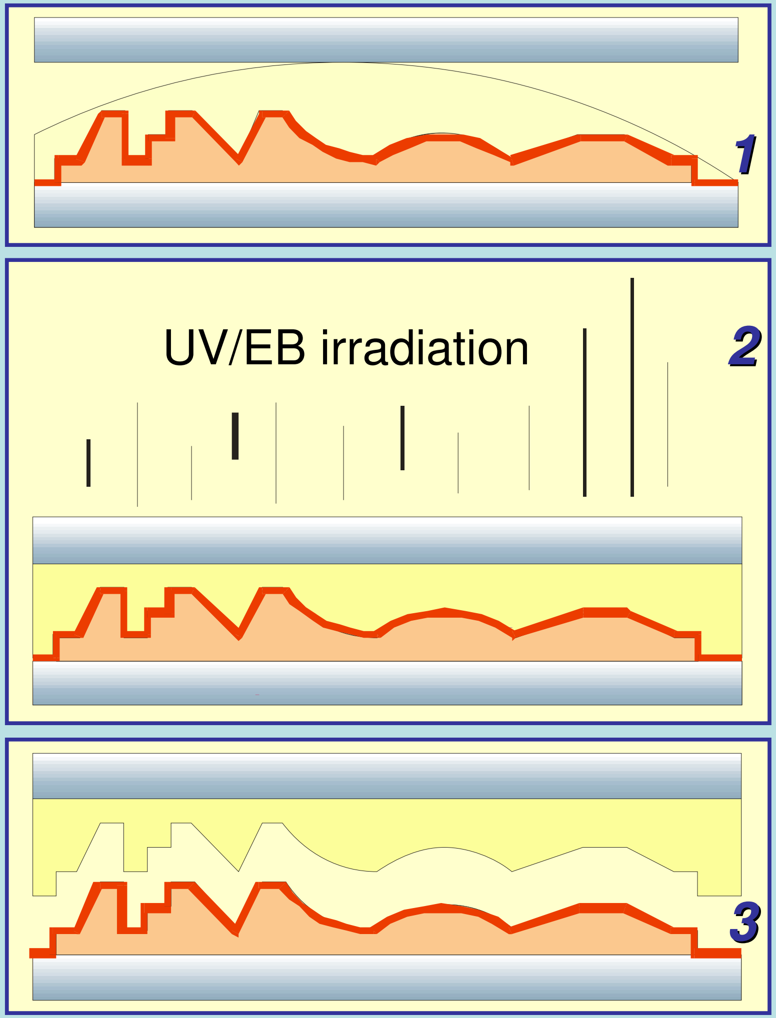
Step 2) Manufacture a tool for producing composite parts

c) Final EB Tool

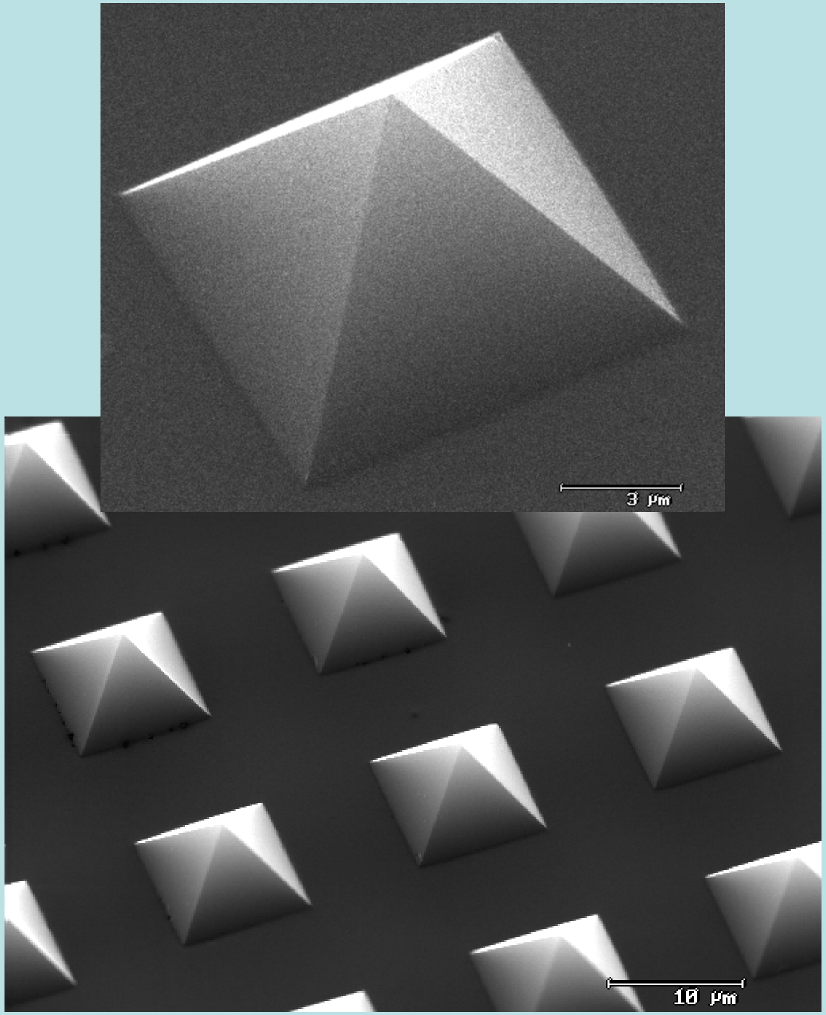



polysiloxane shell:
• radiation curing
• solubility in acrylates
SiO2 nanoparticle:
• mechanical properties
• viscoelastic properties

Applications: Microstructured polyacrylate surfaces



Three steps of the replication process



Application: Irradiation of tubes up to 12 m length (multi-layer-tubes, water supply, gas pipes)

Chain Scissioning

- **Microlithography**
- **LIGA**
- **Polysaccharides**

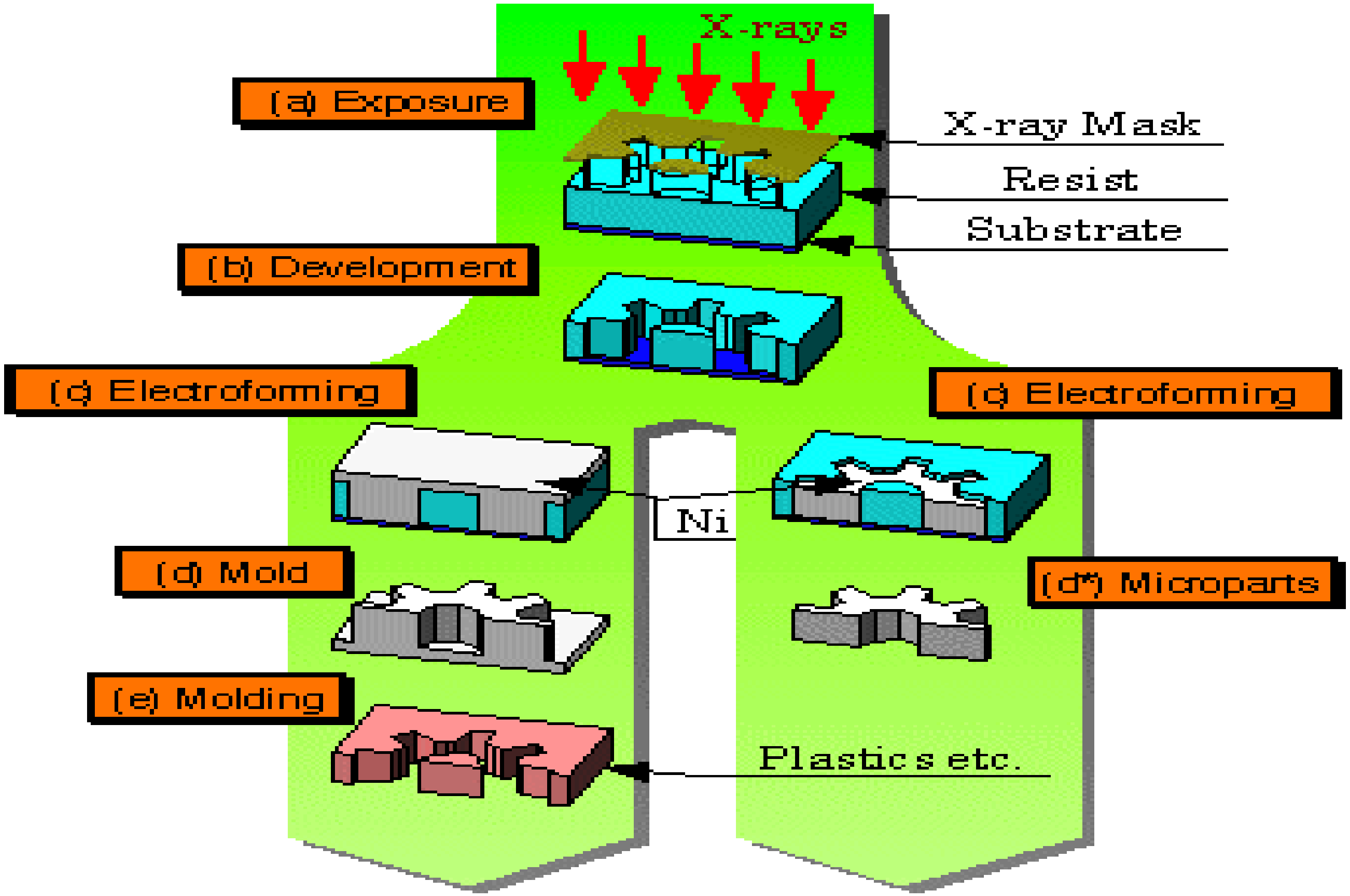
  Plant growth promoters
- **Polymer and Rubber Waste**

  Irradiation of scrap PTFE

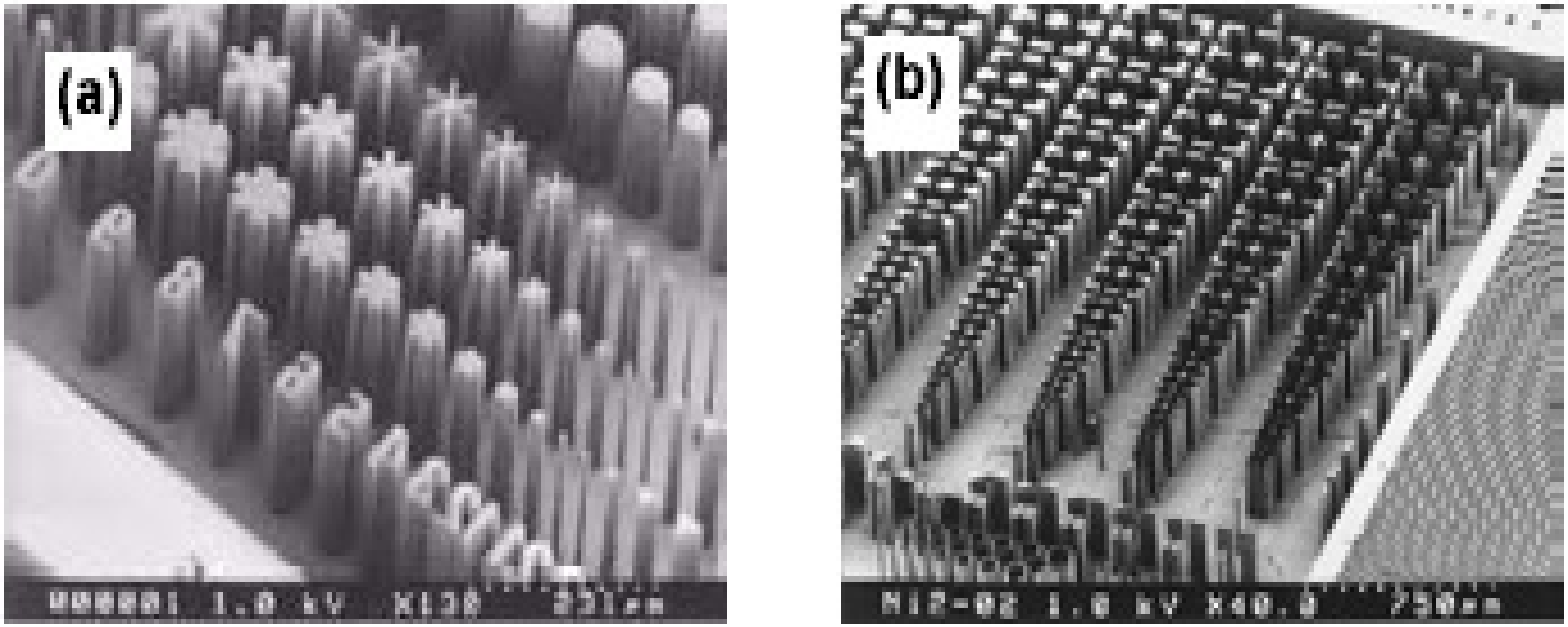
  Recycling of butyl rubber

Electron beam lithography

LIGA Process

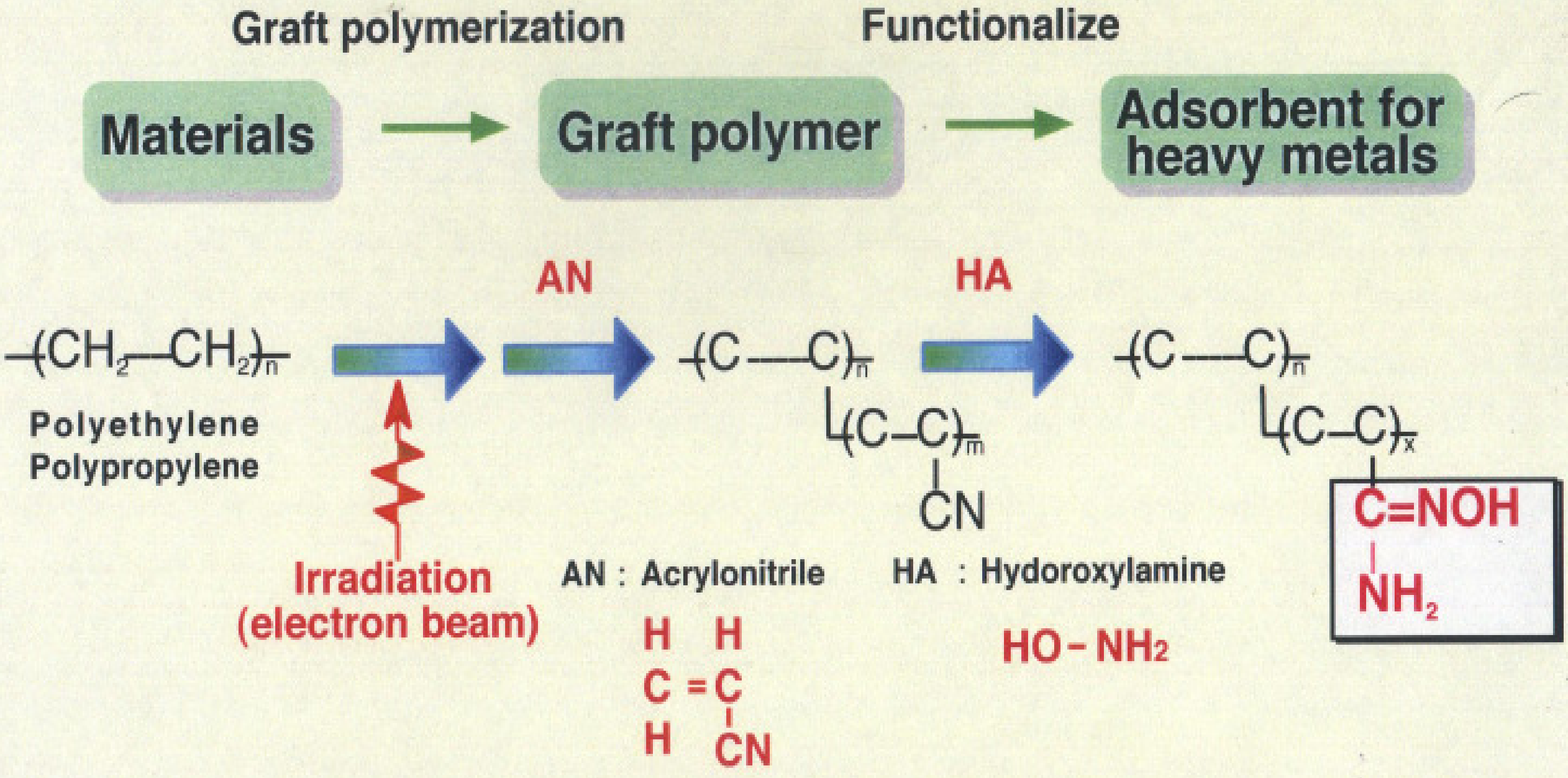


Nanofabrication by LIGA process

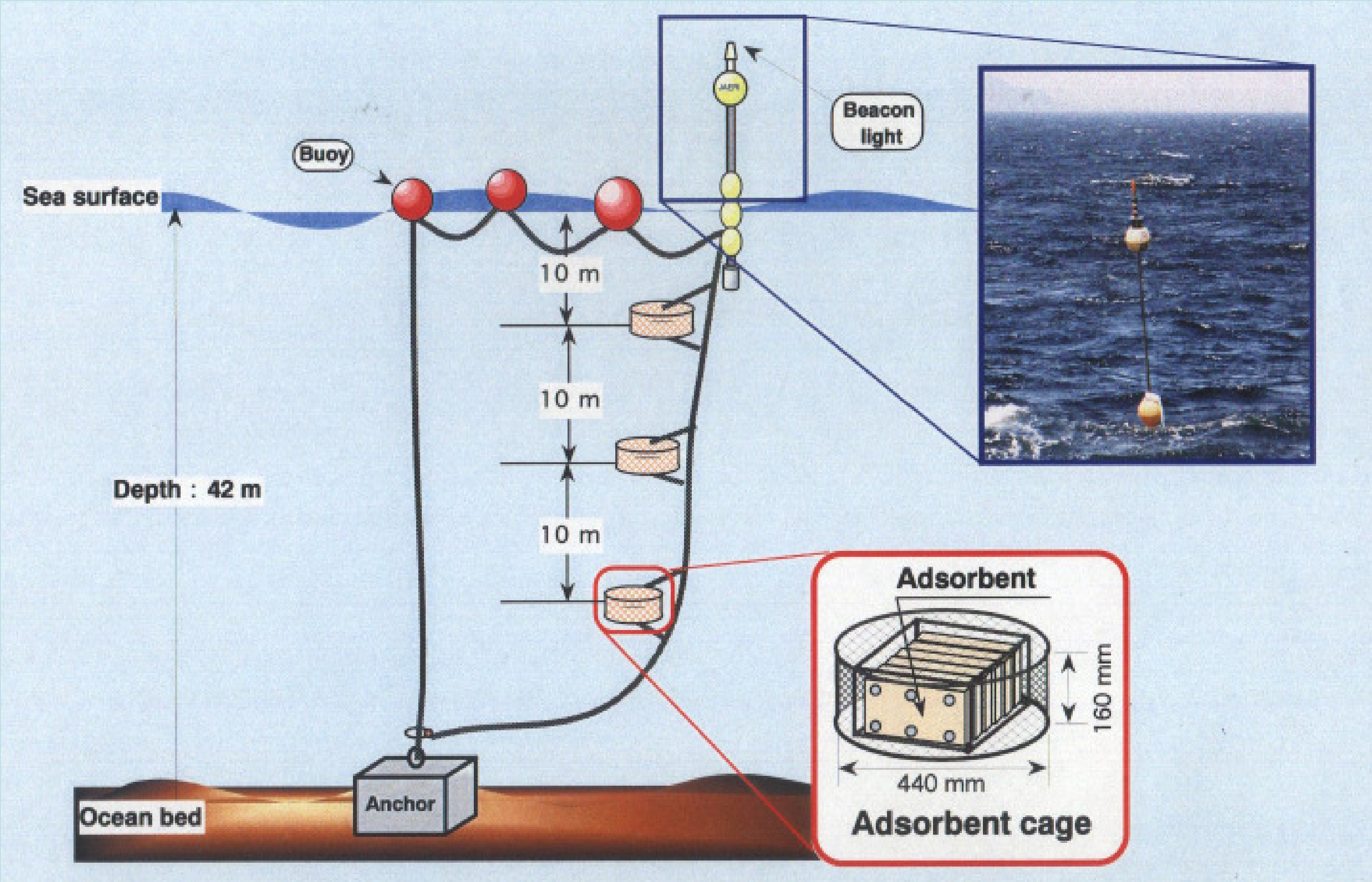


Grafting

- Specialty Adsorbents
- Proton Exchange Membranes
- Nanosurface Modification

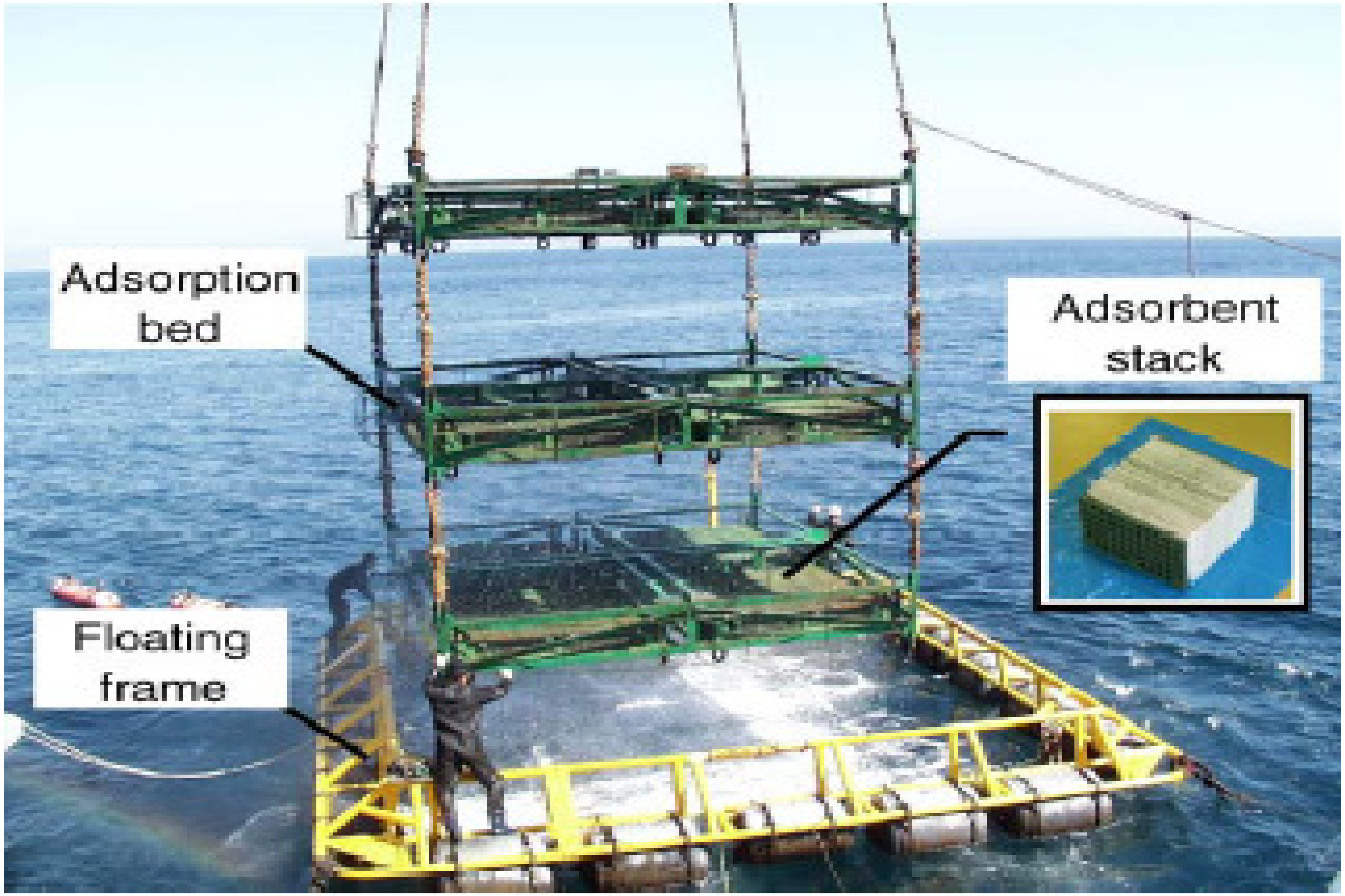


Synthesis of adsorbent for heavy metals by radiation-induced graft polymerization

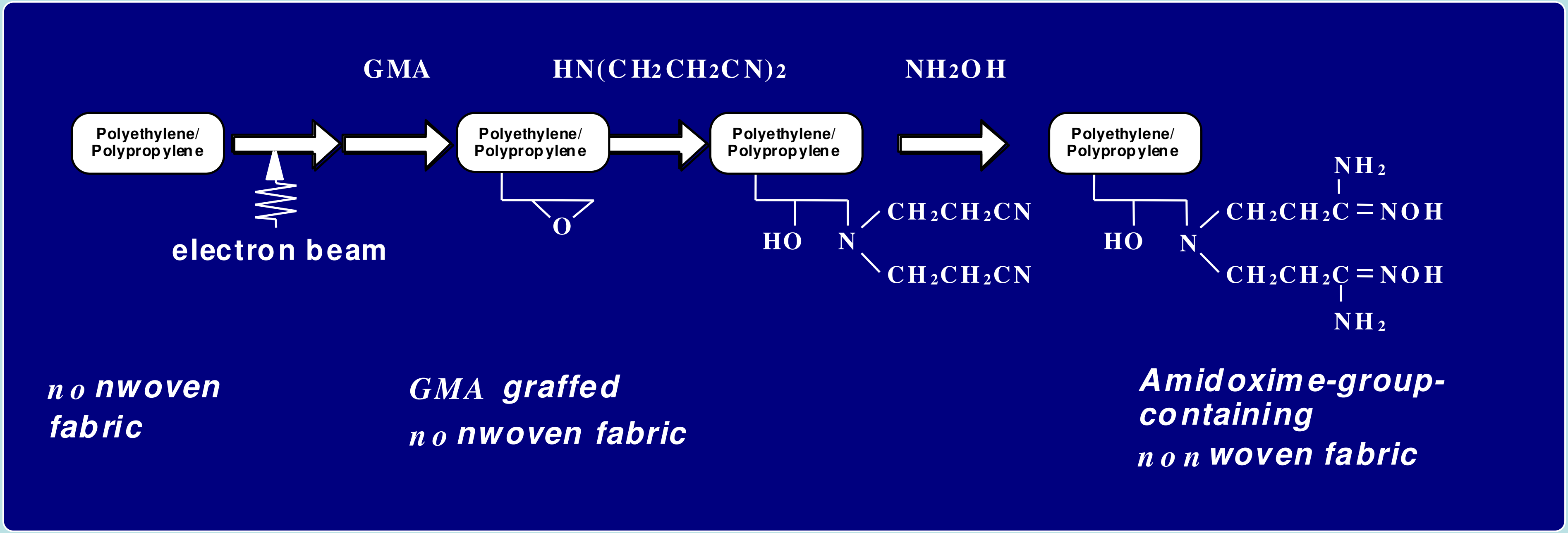


Experiment for Rare Metal Recovery from Seawater

Uranium adsorption from seawater



Schematic preparation of polymeric fabric adsorbent containing two amidoxime groups per repeating unit of grafted chains



The preparation of nonwoven fabric containing surface grafted chains with two amidoxime groups per one monomeric unit requires three steps;

(1) grafting of an epoxy-group containing monomer, glycidyl methacrylate GMA, by pre-irradiation grafting technique,

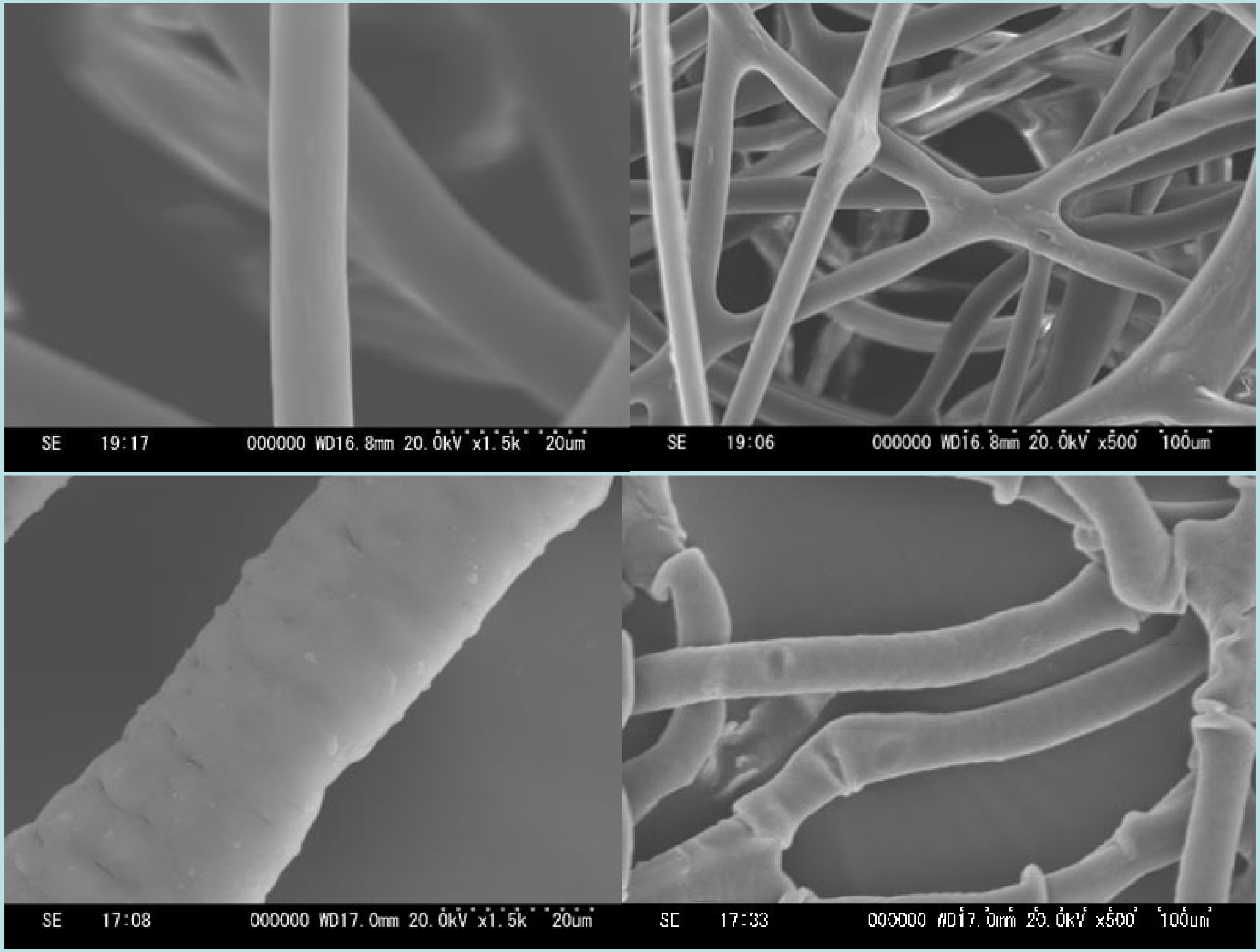
(2) functionalization of epoxy ring with 3,3'-iminodipropionitrile, and

(3) amidoximation reaction of CN groups on the grafted chains.

Characterization by SEM

a

b



Trunk polymer

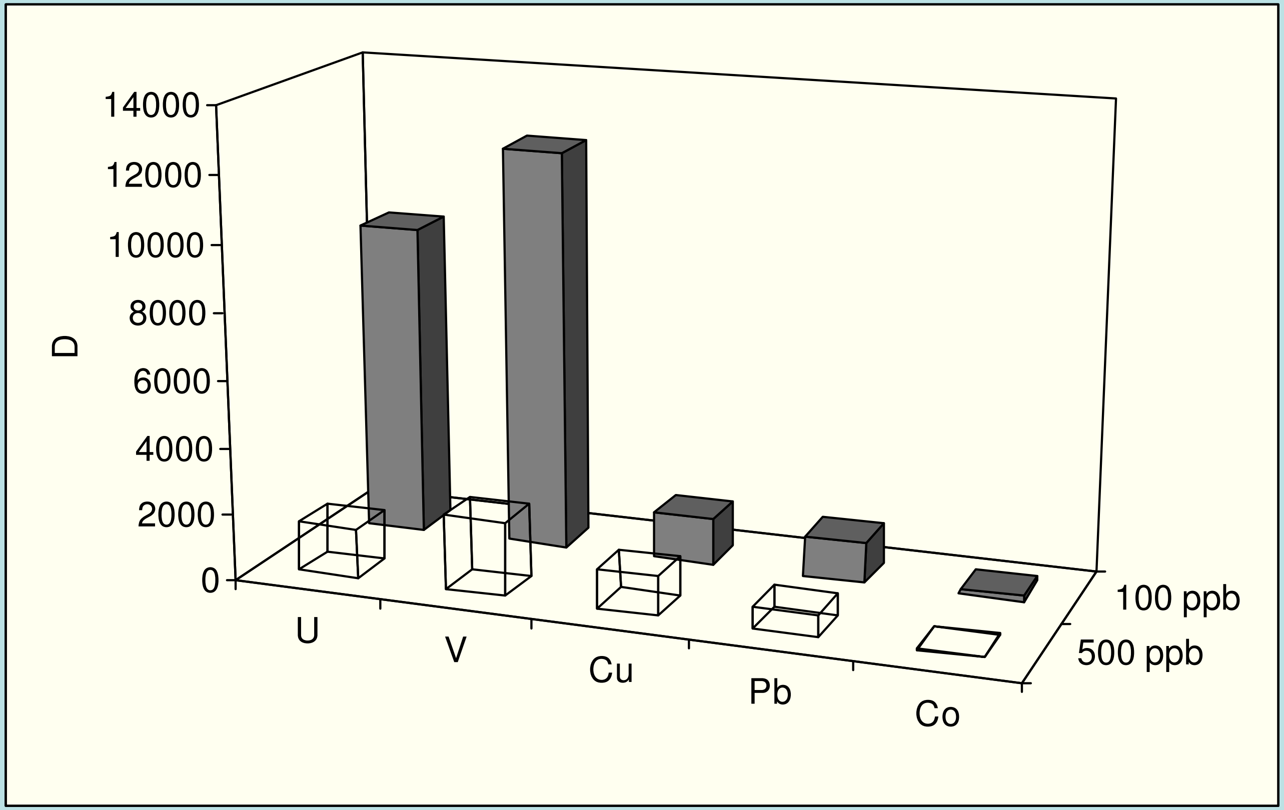
11.6 μm

150 %, GMA grafted fabrics

27.4 μm

SEM photographs of a) trunk non-woven fabric, b) 150 % GMA grafted non-woven fabric, at two different magnifications (1500X and 500X)

Competitive Adsorption



Adsorption selectivity of amidoximated nonwoven fabric for the indicated metal ions at two different initial concentrations

The selectivity expressed as the distribution coefficient (D)

The order of selectivity;

V > U >> Cu ≥ Pb >>Co

These results show that the new adsorbents is suitable for enrichment of trace amounts of U and V ions from seawater or other aqueous media.

A comparison of uranyl ion adsorption using various amidoximated polymeric adsorbents

Research groups	Adsorbent[*]	Uranyl ions adsorbed	Uranyl ions adsorbed normalized to 20 L of total working volume
This work [a]	GMA grafted polypropylene/ polyethylene nonwoven fabrics modified with 3,3'-iminodipropionitrile	0.005 mg/g U 0.0052 mg/g V	2.5 mg/g U 2.6 mg/g V
Egawa[b] et al. (1991)	Lightly crosslinked poly(acrylonitrile-co-divinylbenzene)	650 µg/g U	0.65 mg/g
Suzuki [c] et al. (2000)	Polypropylene nonwoven fabric grafted with acrylonitrile and methacrylic acid	0.576 mg/g U 1.8 mg/g V	0.576 mg/g U 1.8 mg/g V
Kawai[d] et al. (2000)	Polypropylene fabric cografted with methacrylic acid and acryloylchloride	0.2 mg/g U,	0.2 mg/g
Kise[e] et al. (1985)	Dicyanoethylated polystyrene	0.004 mg/g U	0.08 mg/g
Omichi[f] et al. (1986)	Acrylonitrile grafted onto tetrafluoroethylene-ethylene copolymer	0.2 mg/g U	0.08 mg/g
Kabay[g] et al. (1993)	Polypropylene fiber grafted with acrylonitrile	0.152 mg/g U	0.608 mg/g
Takeda[h] et al. (1991)	Acrylonitrile grafted onto porous polyethylene hollow fiber	0.97 mg/g U	0.97 mg/g
Saito[i] et al. (1990)	Acrylonitrile grafted onto porous polyethylene hollow fiber	0.85 mg/g U	0.34 mg/g
Omichi[j] et al. (1985)	Fibrous adsorbent containing acrylic acid and acrylonitrile	0.04 mg/g U	0.08 mg/g

[*] All PAN containing polymers or copolymers are amidoximated

[a] Batch process from 3.3 ppb metal ion mixture solution, volume: 40 mL, the density of amidoxime group (AOD): 2 mmol/g, contact time: 24 h

[b] 0.5 g resin, flow rate: 900 mL/h, seawater volume: 20 L, contact time: 10 days.

[c] 0.07 g amidoxime fiber, the analysis was carried out for amidoxime fiber,which had been immersed in seawater for 30 days. AOD: 6.3 mmol/g

[d] 0.5 g resin, flow rate: 0.47 mL/h, seawater volume: 20 L, contact time: 24 hours. AOD: 3 mmol/g,

[e] 0.1 g resin, seawater volume: 1L, contact time: 96 h,

[f] Semibatch process (5 L of seawater was intermittently exchanged with fresh seawater), total volume: 50 L, contact time: 10 days,

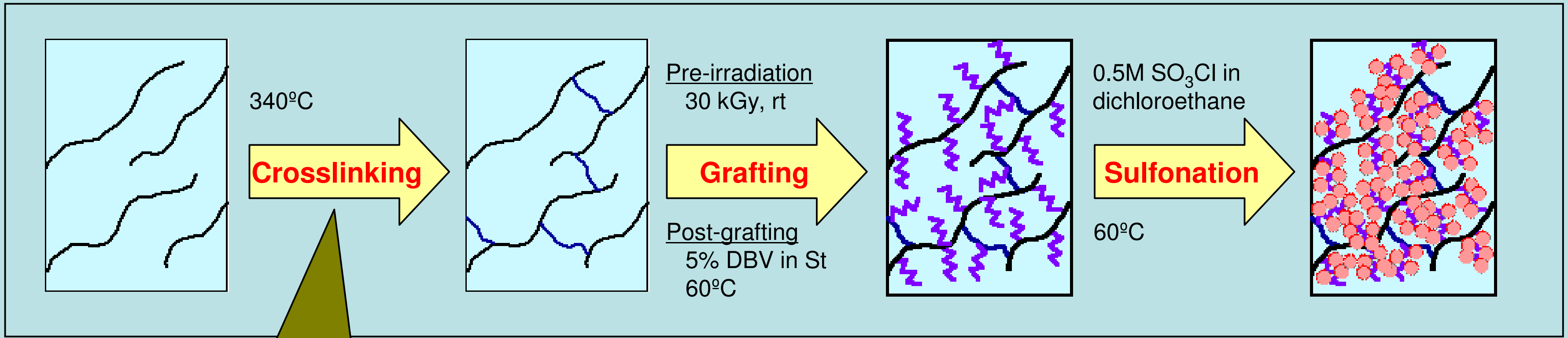
[g] Batch process, seawater volume: 5L, contact time: 24 h,

[h] A continuous-flow experiment, a bundle of 230 AO-H fibers, Contact time: 30 days, AOD: 11.3 mmol/g,

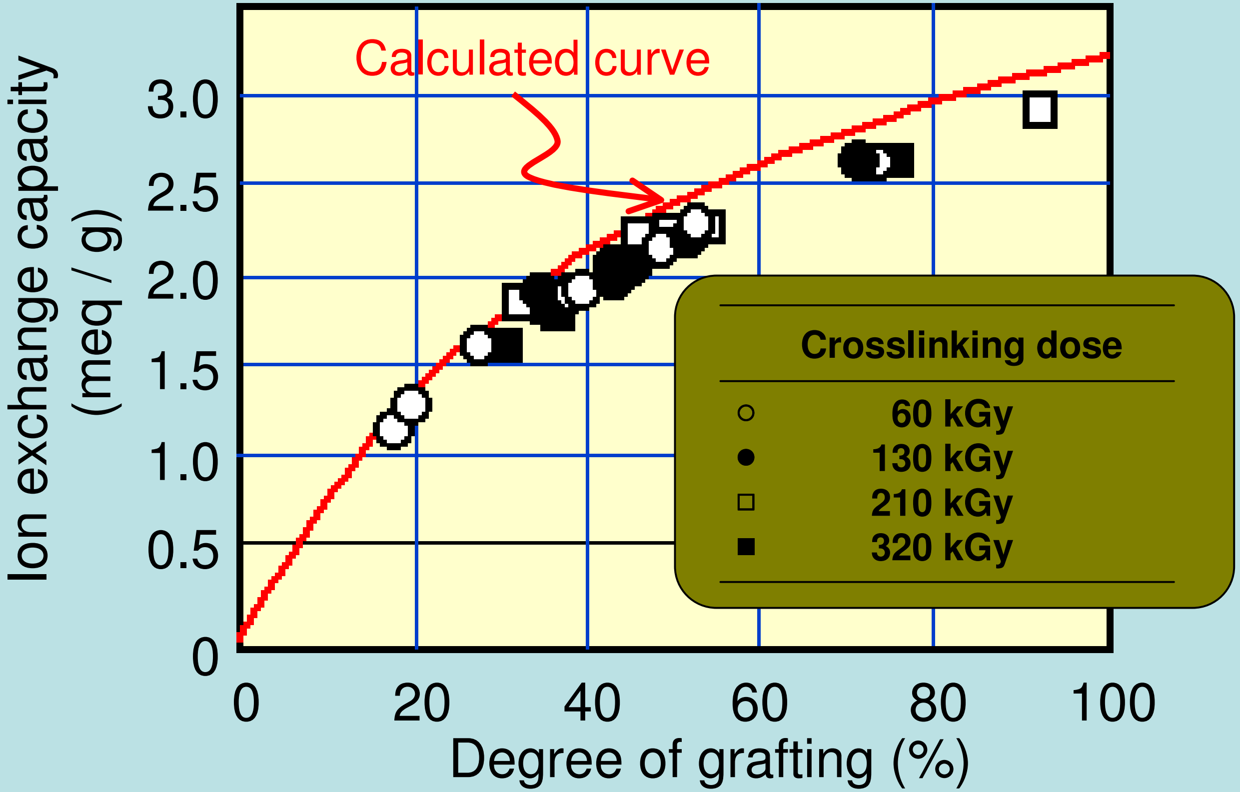
[i] 0.07 g amidoxime membrane, 1 L of seawater was intermittently exchanged with fresh seawater, total volume: 50 L, contact time: 50 days,

[j] 0.1 g resin, semibatch process (2 L of seawater was intermittently exchanged with fresh seawater), total volume: 10 L, contact time: 5 days

Relationship Between Ion Exchange Capacity and Degree of Grafting as a Function of Dose to Crosslink PTFE Film



60 ~ 320 kGy



Calculation of IEC

$$\frac{n(SO_3H)}{W_{dp}} = \frac{1000}{\frac{100Mw}{Y_{graft}} + (Mw + 80)}$$

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