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
Crosslinking of Polyethylene

\[ \text{-C-C-C-C-C-} + e^- = \text{-C-C-C-C-C-} \]
\[ \text{H H H H H} \quad \text{H H H H H} \]

\[ 2 \times \text{-C-C-C-C-C-} \quad \text{Hydrogen Abstracted} \]
\[ \text{H H H H H} \quad \text{H H • H H} \]

\[ \text{-C-C-C-C-C-} \quad \text{Radicals Combine} \]
\[ \text{H H H H H} \quad \text{H H H H H} \]

\[ \text{-C-C-C-C-C-} \quad \text{Crosslinked PE} \]
\[ \text{H H H H H} \quad \text{H H H H H} \]
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°C

Crosslinking condition:

Temperature: 330 - 340°C
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

Dose for crosslinking (kGy)
Wear resistance (relative)
Fig. 2. Delamination associated with oxidation of: (a) UHMWPE tibial knee component and (b) UHMWPE acetabular hip component.
Trapped Radicals in Gamma-irradiated UHMWPE
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.

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

* 10 kilogram (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

Not crosslinked  
crosslinked
Results of the temperature test of connectors out of VESTODUR® X9410

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
Casting solution on plastic film → EB irradiation → Products

FIG. 2.  EB Process for Hydrogel Wound Dressing
Hydrogel Wound Dressing

The graph shows the decrease of wound area (%) over time for two types of dressings: gauze dressing and hydrogel dressing. The y-axis represents the decrease of wound area (%) ranging from 0 to 120, while the x-axis represents the healing time in days ranging from 0 to 14. The hydrogel dressing shows a faster and more significant decrease in wound area compared to the gauze dressing.
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 1.2 m 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
Si\(\text{O}_2\) nanoparticle:
- mechanical properties
- viscoelastic properties

polysiloxane shell:
- radiation curing
- solubility in acrylates
Applications: Microstructured polyacrylate surfaces

Three steps of the replication process:
1. UV/EB irradiation
2. Further steps
3. Resulting surface pattern
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
Nanofabrication by LIGA process
Grafting

- Specialty Adsorbents
- Proton Exchange Membranes
- Nanosurface Modification
Graft polymerization → Functionalize

Materials → Graft polymer → Adsorbent for heavy metals

Polyethylene or Polypropylene → Irradiation (electron beam) → Acrylonitrile (AN) → Hydoroxylamine (HA) → Adsorbent for heavy metals

AN: Acrylonitrile
HA: Hydoroxylamine

Synthesis of adsorbent for heavy metals by radiation-induced graft polymerization
Experiment for Rare Metal Recovery from Seawater
Uranium adsorption from seawater
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.
SEM photographs of a) trunk non-woven fabric, b) 150 % GMA grafted non-woven fabric, at two different magnifications (1500X and 500X)

- Trunk polymer
  - 11.6 µm
- 150 %, GMA grafted fabrics
  - 27.4 µm
Adsorption selectivity of amidoximated nonwoven fabric for the indicated metal ions at two different initial concentrations

The order of selectivity:

\[ V > U >> Cu \geq Pb >> Co \]

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

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

* All PAN containing polymers or copolymers are amidoximated.

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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: 1 L, 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: 5 L, 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

Crosslinking

Pre-irradiation
30 kGy, rt

Grafting
Post-grafting
5% DBV in St 60°C

Sulfonation
0.5M SO₂Cl in dichloroethane 60°C

Calculation of IEC:

\[
\frac{n(\text{SO}_3\text{H})}{W_{dp}} = \frac{1000}{100M_w \gamma_{\text{graf}}} + (M_w + 80)
\]

Crosslinking dose:
- 60 kGy
- 130 kGy
- 210 kGy
- 320 kGy

Ion exchange capacity (meq/g)

Degree of grafting (%)

Calculated curve
Acknowledgement