Compounding and Manufacturing Elastomers for Nuclear Applications

Polymers in nuclear applications 2019
Andrew Douglas FIMMM
James Walker Overview

Centres of Excellence
Materials Technology and Manufacture

- Advanced Engineered Plastics
- Precision Machined Metals
- High Performance Elastomers
- Innovative Bolting Technology
- Vibration Attenuation

- 2000 employees / £200m turnover
- Established 1882
- 16 manufacturing sites
- 35 sales / support offices
What is an Elastomer?
The concept of polymers
Polymer structure
Polymer structure with crosslinks
The history of natural rubber
The development of synthetic rubbers and compounding
Designing synthetic polymers...

Monomers & Polymers

Attributes of monomer ‘building blocks’

- **Strength** of bonds within molecules and between them
- **Highly polar** gives resistance to swelling by oils/fuels
- **Flexibility** at low temperatures
Synthetic Polymers
How long will it last?

‘All of the disputed territories contain valuable minerals, and some of them yield important vegetable products such as rubber which in colder climates it is necessary to synthesize by comparatively expensive methods’

Nineteen Eighty-Four, George Orwell, first published June 1949

Synthetic elastomers haven’t actually been around for that long so

100 year life predictions come with caveats…”
GENERAL ELASTOMER CLASSIFICATION

General Purpose
Low oil resistance

General Purpose
Oil Resistant

High Performance

Natural
Chloroprene
Ethylene-Propylene
Fluorocarbon
Silicone
HNBR
Aflas®
Acrylic
Polyurethane
Nitrile
Natural Rubber (NR)

Cis-1,4-polyisoprene

Advantages: High resilience; high tensile/tear; good abrasion resistance; low cost.

Disadvantages: Poor oil resistance; poor weathering resistance. Reversion.

Typical temperature range: -50°C to +100°C
Ethylene-Propylene Rubber (EPM, EPDM)

Dipolymer of ethylene and propylene (EPM), or Termonomer of ethylene-propylene with a diene monomer

\[
\begin{align*}
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{H} & \text{C} \\
\text{C} & \text{H}
\end{align*}
\]

+ diene monomer in EPDM

Diene monomer (EPDM) allows us to cure with sulphur as well as peroxides

**Advantages:** Excellent ozone/weathering resistance. Excellent radiation, hot water and steam resistance (peroxide grades); good resistance to inorganic and polar organic chemicals.

**Disadvantages:** Low resistance to hydrocarbons.

**Typical temperature range:** -45°C to +150°C (-49°F to +300°F).
Polychloroprene (Neoprene) Rubber (CR)

2-chlorobutadiene

Advantages: Good weather and ozone resistance; good mechanicals; resistance to many Freons; some oil resistance; low cost.
Disadvantages: Only moderate oil resistance; limited temperature resistance.
Typical temperature range: -40°C to +120°C (-40°F to +250°F)
Nitrile Rubber (NBR)

*Acrylonitrile-butadiene*

![Chemical structure of Nitrile Rubber](image)

**Typical temperature range:** -50°C to +120°C (dependent on ACN content!)
Hydrogenated Nitrile Rubber (HNBR/HSN)

Made from NBR by hydrogenation reaction

Typical temperature range: -40°C to +160°C (dependent on ACN content!)
Fluoroelastomers (FKM/FPM)


Vinylidene fluoride, VDF (VF₂)  Hexafluoropropylene, HFP  Tetrafluoroethylene, TFE  Cure site monomer, CSM

Dipolymers, VDF and HFP, ~66%F (‘A’ Types)
Terpolymers*, VDF, HFP, TFE (CSM) ~68%F to ~70%F FKM (‘B’ types at 68%F and ‘F’types at 70%F).

Typical temperature range: -45°C to +200°C
Aflas® (TFE-P / FEPM)

Tetrafluoroethylene-propylene

Advantages: Excellent ozone/weathering resistance; good heat resistance; excellent resistance to steam and radiation; good overall chemical resistance.

Disadvantages: High compression set; high Tg; poor resistance to aromatics

Typical temperature range: 0°C to +200°C
RELATIVE BASE POLYMER COSTS...
What goes in to an elastomer?

Protective system

Cure system
<table>
<thead>
<tr>
<th></th>
<th>Compound Ingredient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>POLYMERS</td>
</tr>
<tr>
<td>2</td>
<td>CURATIVES</td>
</tr>
<tr>
<td>3</td>
<td>ACCELERATORS</td>
</tr>
<tr>
<td>4</td>
<td>ACTIVATORS</td>
</tr>
<tr>
<td>5</td>
<td>RETARDERS</td>
</tr>
<tr>
<td>6</td>
<td>CO-AGENTS</td>
</tr>
<tr>
<td>7</td>
<td>FILLERS</td>
</tr>
<tr>
<td>8</td>
<td>PLASTICISERS</td>
</tr>
<tr>
<td>9</td>
<td>EXTENDERS</td>
</tr>
<tr>
<td>10</td>
<td>PROTECTANTS</td>
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<tr>
<td>11</td>
<td>BONDING PROMOTERS</td>
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<tr>
<td>12</td>
<td>PROCESS AIDS</td>
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<tr>
<td>13</td>
<td>TACKIFIERS</td>
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<tr>
<td>14</td>
<td>DESICCANTS</td>
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<tr>
<td>15</td>
<td>PIGMENTS</td>
</tr>
<tr>
<td>16</td>
<td>BLOWING AGENTS</td>
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<tr>
<td>17</td>
<td>PEPTISERS</td>
</tr>
<tr>
<td>18</td>
<td>FLAME RETARDANTS</td>
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<tr>
<td>19</td>
<td>ODOURANTS</td>
</tr>
<tr>
<td>20</td>
<td>COUPLING AGENTS</td>
</tr>
<tr>
<td></td>
<td>High Quality</td>
</tr>
<tr>
<td>----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>34% ACN NBR</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
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<tr>
<td>Stearic acid</td>
<td>1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1</td>
</tr>
<tr>
<td>Accelerators</td>
<td>4</td>
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<tr>
<td>Ester plasticiser</td>
<td>7</td>
</tr>
<tr>
<td>AO₂ / AO₃</td>
<td>2</td>
</tr>
<tr>
<td>Carbon black N550</td>
<td>70</td>
</tr>
<tr>
<td>Oil extender</td>
<td>-</td>
</tr>
<tr>
<td>Chalk Dust</td>
<td>-</td>
</tr>
<tr>
<td>Talcum Powder</td>
<td>-</td>
</tr>
<tr>
<td>White filler</td>
<td>-</td>
</tr>
<tr>
<td>Wax</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total PHR</strong></td>
<td><strong>190</strong></td>
</tr>
<tr>
<td>Property</td>
<td>High Quality</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Cure</td>
<td>6 minutes at 180°C</td>
</tr>
<tr>
<td>Hardness (IRHD)</td>
<td>78</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>19.3</td>
</tr>
<tr>
<td>E @ B (%)</td>
<td>300</td>
</tr>
<tr>
<td>Modulus at 25% strain (MPa)</td>
<td>1.3</td>
</tr>
<tr>
<td>Modulus at 50% strain (MPa)</td>
<td>2.2</td>
</tr>
<tr>
<td>Modulus at 100% strain (MPa)</td>
<td>4.8</td>
</tr>
<tr>
<td>Tear strength (N/mm)</td>
<td>42</td>
</tr>
<tr>
<td>Compression Set, 24hr @ 70°C (%)</td>
<td>7</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.2</td>
</tr>
</tbody>
</table>
One piece of rubber looks pretty much like another....
Elastomer behaviour at low temperatures

- Decrease in energy
- Polymer chains lose flexibility
- ‘Leathery phase’ before taking on the properties of glass
- Properties vary depending on the polymer type/formulation
Elastomer behaviour at high temperatures

- Long-term resistance influenced by strength of bonds between atoms
- Stronger bonds permit higher operating temperatures
- Mechanical properties will reduce
Swelling

- Elastomer will absorb the contact media and swell
- Physical effect, which is to some extent reversible

Chemical Attack

- Polymer chain is altered / attacked by the contact media
- Irreversible

Elastomer behaviour in contact media

Can occur at the same time
Mechanico-oxidative fatigue

Ozone cracking

Heat and oxidation

Crosslink reversion

Sunlight crazing

Chemical attack

Abrasion

Compression set at high temperature
Environmental Qualification

Fixed formulations – fantastic

But…

Legacy materials – availability of raw ingredients
Shieldseal® 661, 663 and 664 Elastomers

Radiation testing carried out by Wood Group

- Exposure to gamma radiation
- $1 \text{kGy/hr}^{-1}$ up to 1000 kGy
- Followed by further 600 kGy
- Aged and unaged samples
- Intended to replicate LOCA – broadly based on IEEE 383 / IEC 60780 standards
Accelerated Thermal Ageing
Potential impact of variations in Activation Energy

Victoria Smith Wood Group EQSA Seminar Sept 2019
Martin Baker – Ejector seats – O
Thank you!

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