Effect of Electron Beam Irradiation on Structure and Properties of Styrene-Butadiene Rubber

Katarzyna S. Bandzierz, Louis A.E.M. Reuvekamp, Grażyna Przybytniak, Wilma K. Dierkes, Anke Blume, Dariusz M. Bielinski

INTERNATIONAL RUBBER CONFERENCE (IRC), KUALA LUMPUR, 4th – 6th September 2018
Crosslinking Density

- Tear Strength
- Toughness
- Fatigue Life
- High Speed
- Dynamic Modulus
- Static Modulus
- Hardness
- Tensile Strength
- Hysteresis
- Permanent Set
- Friction Coefficient

In-Rubber Properties

Crosslinking Density

[Crosslinking Density (mol/cm^3)]

low

high
Sulfur Curing

Disadvantage of sulfur curing:

- Presence of
  - double bond
  - Sulfur + accelerator in the compound
- 130 – 160 °C required
- Variety in crosslinks

INTERMOLECULAR CROSSLINKS
- elastically effective

INTRAMOLECULAR CROSSLINKS
- Cyclic structures
- Pendant groups
Peroxide Curing

Disadvantage of peroxide curing:

- Presence of peroxides in the compound
- 130 – 160 °C required

\[
R-O-O-R' \rightarrow R-O^* \quad + \quad *O-R' + \text{Heat}
\]

\[
RO^* \rightarrow R^* + O_2
\]

\[
R^* + \quad \rightarrow \quad R^*
\]
Alternative crosslinking method: Radiation Curing

**Electron beam** — beam of high-energetic, accelerated electrons generated in electron accelerator

Ionizing radiation - ENERGY

Secondary electron
Radiation Curing

Alternative crosslinking method: Radiation Curing

- Independent of
  - double bonds
  - curing system
- Curing at room temperature is possible
Radiation Curing

- Curatives are not necessary
- Process initiated by high-energy ionizing radiation

C-C crosslink between polymer chains

Degradation of the polymer
But which radiation dose is the best for a good performance of the created network?
Radiation Curing

Styrene-butadiene rubber (SBR)

- E-SBR; KER 1500, Synthos (Poland);
  23.5% of bound styrene
- $M_w = 425\,000\,g/mol$

- Irradiation with doses: 25, 50, 75, 100, 150, 200 kGy
- Electron beam:
  - energy of 10 MeV
  - average power of 10 kW
- Irradiation conditions:
  - air atmosphere at room temperature

Reference sample: non-irradiated
Radiation curing leads to:

- C-C crosslink between polymer chains
- Degradation of the polymer

Charlesby-Rosiak tried to quantify both reactions by sol-gel analysis
Sol-Gel Analysis

0.2 g rubber extracted with THF (30 days) – drying at 60 °C (7 days):

→ insoluble (gel) fraction

→ soluble (sol) fraction

Soxhlet extractor
Chain scission vs crosslinking

Charlesby-Rosiak:

\[ s + \sqrt{s} = \frac{p_0}{q_0} + \left(2 - \frac{p_0}{q_0}\right)\left(\frac{D_v + D_g}{D_v + D}\right) \]

\[ p_0/q_0 = 0.24 \]

\[ p_0 \] – average chain scission density per radiation dose unit
\[ q_0 \] – average crosslinking density per radiation dose unit
\[ D \] – radiation dose
\[ D_v \] – virtual dose
\[ D_g \] – gel dose

s – sol fraction

average chain scission density / average crosslinking density = ca. 1 : 4
Effect of ionizing radiation on gel formation: gel fraction

Higher irradiation leads to higher insoluble (gel) fraction - crosslink density
Samples swollen in toluene for 4 days at RT, dried 4 days at 60 °C, calculation according to Flory-Rehner.

New chemical bonds are formed mainly between already crosslinked polymer chains at higher doses.
Crosslink density

Samples swollen in toluene for 4 days at RT, dried 4 days at 60 °C, calculation according to Flory-Rehner

Samples swollen in toluene for 4 days at RT, dried 4 days at 60 °C, swollen in cyclohexane for 4 days at RT, **freezing point depression** evaluated by DSC (heating rate 5 K/min)

What happens at higher dosage rates?
Crosslink density


What happens at higher dosage rates?
Gel fraction vs crosslink density


What happens at higher dosage rates?
Polymer degradation becomes more likely!
Effect of ionizing radiation on SBR structure: mechanical properties

- Higher crosslinks lead to higher hardness
- Few crosslinks lead to significant increase in modulus
Effect of ionizing radiation on SBR structure: mechanical properties

- Maximum tensile strength: ca. for 100 kGy
- Few crosslinks lead to significant reduction of EaB
Summary

• SBR can be cured by radiation

• Radiation dose influences crosslink density

• Increasing crosslink density influences hardness and stress-strain behavior
Summary

Which radiation dose is the best for a good performance of the created network?

- Required radiation dose for sufficient SBR crosslinking network ca. 150 kGy
- Charlesby-Rosiak model is applicable for radiation-curing process
- Chain scission density / Crosslinking density = ca. 1 : 4
Acknowledgements

Thanks to the Ministry of Science and Higher Education (Republic of Poland) for the financial support.
Thank you for your kind attention!

katarzyna.bandzierz@gmail.com
a.blume@utwente.nl

This paper is already published in:
Radiation Curing

Radiation curing leads to:

- C-C crosslink between polymer chains
- Degradation of the polymer

1959: Charlesby and Pinner tries to quantify both reactions by sol-gel analysis
0.2 g rubber extracted with THF (30 days) – drying at 60 °C (7 days):
→ insoluble (gel) fraction
→ soluble (sol) fraction

Soxhlet extractor
Sol-Gel Analysis

Charlesby-Pinner equation

\[ s + \sqrt{s} = \frac{p_0}{q_0} + \frac{2}{q_0 u_{2,0} D} \]

- \( s \) – sol fraction
- \( p_0 \) – average chain scission density per radiation dose unit
- \( q_0 \) – average crosslinking density per radiation dose unit
- \( u_{2,0} \) – average degree of polymerization of the primary polymer chains
- \( D \) – radiation dose
Assumptions:

- Chain scission and crosslinking occur at random spatial distribution and proportionally to radiation dose.
- Ratio between chain scission and crosslinking is constant over the whole range of doses.
- Crosslinking leads to formation of tetra-functional crosslinks $X$, not tri-functional endlinks $Y$.
- Initial molecular weight distribution is random:

  \[
  \text{polydispersity index PDI} = \frac{\overline{M}_w}{\overline{M}_n} = 2
  \]

  \[
  (\overline{M}_w - \text{weight-average molecular weight}, \quad \overline{M}_n - \text{number-average molecular weight})
  \]
Chain scission vs crosslinking

Charlesby-Pinner equation

\[ s + \sqrt{s} = \frac{p_0}{q_0} + \frac{2}{q_0 u_{2,0} D} \]

\[ \frac{1}{D} \text{ / kGy}^{-1} \]

\[ \frac{M_w}{M_n} > 2 \]

\[ \frac{M_w}{M_n} = 2 \]

\[ \frac{M_w}{M_n} < 2 \]

\[ \rightarrow \text{Limitation of this model if } \frac{M_w}{M_n} \neq 2 \]
Chain scission vs crosslinking

→ Limitation of this model if $\frac{\bar{M}_w}{\bar{M}_n} \neq 2$

Charlesby-Pinner equation

NO linear correlation!

\[ \frac{\bar{M}_w}{\bar{M}_n} > 2 \]

(GPC: PDI = $\frac{\bar{M}_w}{\bar{M}_n} = 2, 8$)
Chain scission vs crosslinking

→ Limitation of Charlesby-Pinner if \( \frac{\bar{M}_w}{\bar{M}_n} \neq 2 \)

Charlesby-Rosiak equation

\[
s + \sqrt{s} = \frac{p_0}{q_0} + \left( 2 - \frac{p_0}{q_0} \right) \left( \frac{D_v + D_g}{D_v + D} \right)
\]

- \( s \) – sol fraction
- \( p_0 \) – average chain scission density per radiation dose unit
- \( q_0 \) – average crosslinking density per radiation dose unit
- \( D \) – radiation dose
- \( D_v \) – virtual dose
- \( D_g \) – gel dose
Effect of ionizing radiation on SBR structure: DSC glass transition temperature ($T_g$)

Increase of $T_g$: formation of crosslinks

Decrease of $T_g$: chain scissions
Yield of chain scission ($G_s$) and crosslinking ($G_x$)

Condition for effective crosslinking: $G_s/G_x < 4$

<table>
<thead>
<tr>
<th>Investigated</th>
<th>$G_s/G_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>0.49</td>
</tr>
<tr>
<td>cis-1,4 BR [1]</td>
<td>0.10</td>
</tr>
<tr>
<td>EPDM [2]</td>
<td>0.26</td>
</tr>
</tbody>
</table>

- SBR, BR and EPDM can be crosslinked by irradiation
- Irradiation of SBR leads to higher chain scission than in EPDM or BR

Effect of ionizing radiation on SBR structure

Why does the irradiation of SBR leads to higher chain scission than in EPDM or BR?

- styrene ring absorbs radiation – dissipate it = more resistant to crosslinking but also to degradation
- styrene blocks stiffen the polymer chain = crosslinking is less likely

Ionizing radiation - ENERGY

23.5% of bound styrene

- C, CH, CH_2, C, H_2 

* 

n 

m
Influence of styrene content on crosslinking ($G_x$)

Used E-SBR; KER 1500, Synthos (Poland); 23.5% of bound styrene

<table>
<thead>
<tr>
<th></th>
<th>$G_x$ in µmol / J [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR (16% of styrene)</td>
<td>0.30</td>
</tr>
<tr>
<td>SBR (28% of styrene)</td>
<td>0.16</td>
</tr>
<tr>
<td>SBR (85% of styrene)</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Increasing amount of styrene hinders crosslinking.