Guayule Rubber Radiation Attenuation Medical Glove

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Radiation Attenuation Gloves & Fluoroscopy Assisted Surgeries

• Fluoroscopy
  A continuous X-ray beam is passed through the body part being examined. The beam is transmitted to a monitor so the body part and its motion can be seen in detail.

• Surgeries requiring intraoperative fluoroscopy
  Traumatology, Orthopedic, Cardiovascular, etc.
  NCRP 2006 – 16 million cases
Radiation Attenuation Gloves & Fluoroscopy Assisted Surgeries

• Radiation exposure to hand
  • Directly under radiation source
  • Highest exposure, less protected (than other body parts)

• Known outcomes
  • Radiation dermatitis and skin damage
  • Stochastic effects

• Radiation attenuation gloves
  • Embedded radiation shielding material to reduce exposure
  • Up to 40% reduction
### Existing RA gloves

**Failing at tensile performances**

<table>
<thead>
<tr>
<th>Glove Brand</th>
<th>Basic Info</th>
<th>Tensile Performance</th>
<th>Attenuation %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base Polymer</td>
<td>Attenuat. agent</td>
<td>Thickness (mm)</td>
</tr>
<tr>
<td><strong>ASTM Standard</strong>*</td>
<td>Exam I (natural)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ProGuard</td>
<td>HNR</td>
<td>PbO</td>
<td>0.32</td>
</tr>
<tr>
<td>RadiaXon</td>
<td>HNR</td>
<td>Bi$_2$O$_3$</td>
<td>0.38</td>
</tr>
<tr>
<td>XP</td>
<td>HNR</td>
<td>PbO</td>
<td>0.40</td>
</tr>
<tr>
<td>Ansell</td>
<td>HNR</td>
<td>Bi$_2$O$_3$</td>
<td>0.30</td>
</tr>
<tr>
<td>Kiran</td>
<td>HNR</td>
<td>Bi+other</td>
<td>0.35</td>
</tr>
<tr>
<td><strong>ASTM Standard</strong>*</td>
<td>Exam II (synthetic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBI</td>
<td>CR</td>
<td>W</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Specs collected from manufacturer and vendor websites.

* For Tensile, ASTM D3578, Exam I (natural), or Exam II (synthetic); For Attenuation, ASTM D7866

Not medical gloves
Radiation Attenuation Gloves

The Problem

• Manufacturers
  • Diluent attenuation fillers reduce mechanical performances of RA gloves to < FDA requirement
  • FDA requires double-gloving (RA + medical) to protect against both radiation and pathogens

• End-users
  • Stiff RA glove + double gloving = unpopular
  • Reduced tactile sensation, increased hand fatigue
  • Loss of hand dexterity
# Our Goal

Exam and/or Surgical, RA glove

## Natural Rubber Surgical and Examination Gloves

<table>
<thead>
<tr>
<th>Standard #</th>
<th>Polymer Type</th>
<th>Thickness (mm) (minimum)</th>
<th>Tensile Strength (MPa) (minimum)</th>
<th>Ultimate Elongation (%) (minimum)</th>
<th>Modulus at 500% strain (MPa) (Maximum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D3577</td>
<td>Surgical I (natural)</td>
<td>0.10</td>
<td>24</td>
<td>750</td>
<td>5.5</td>
</tr>
<tr>
<td>ASTM D3578</td>
<td>Exam I (natural)</td>
<td>0.08</td>
<td>18</td>
<td>650</td>
<td>5.5</td>
</tr>
</tbody>
</table>


## Radiation Attenuating Protective Gloves

<table>
<thead>
<tr>
<th>ASTM D7866</th>
<th>Energy Levels</th>
<th>60 kVp</th>
<th>80 kVp</th>
<th>100 kVp</th>
<th>120 kVp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum attenuation</td>
<td>29%</td>
<td>22%</td>
<td>18%</td>
<td>15%</td>
</tr>
</tbody>
</table>

[https://www.astm.org/Standards/D7866.htm](https://www.astm.org/Standards/D7866.htm)
Our Solution
Guayule Natural Rubber (GNR)

- More linearity of rubber molecules (low to no branching)
  - More elasticity and softness at comparable strength (vs HNR).
  - Improved polymer-filler interactions (filler loading has less impact on mechanical performance).
# Experimental Design Variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
<th>Unit</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$O$_3$</td>
<td>120</td>
<td>150</td>
<td>phr</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.25</td>
<td>0.34</td>
<td>phr</td>
</tr>
<tr>
<td>Water</td>
<td>20</td>
<td>50</td>
<td>phr</td>
</tr>
<tr>
<td>Former Types</td>
<td>thin</td>
<td>thick</td>
<td>Aluminum alloy plate formers for film samples.</td>
</tr>
<tr>
<td>Film Thickness</td>
<td>0.24</td>
<td>0.31</td>
<td>mm</td>
</tr>
<tr>
<td>Cure temp</td>
<td>70</td>
<td>105</td>
<td>°C</td>
</tr>
<tr>
<td>Cure time</td>
<td>35</td>
<td>105</td>
<td>min</td>
</tr>
</tbody>
</table>

120 phr Bi$_2$O$_3$ at 0.28 mm film thickness could provide the minimum attenuation required by ASTM-D7866.
Experimental Design

Tensile testing method

• A total of 84 film samples
• ASTM D412 testing specification
  • Die “C” for specimen cutting
  • 5 specimens per sample

• Instron 3366 + Epsilon 3800
  • Blue hill v2 program

• Changes in formulation and curing conditions were made according to results from earlier experiments.
Result 1

Appearance of GNR-Bi$_2$O$_3$ films

Under-cured films are light yellow to light brown.

Fully cured GNR-Bi$_2$O$_3$ films are medium to dark brown in color.
Result 2
Former Difference

- Two types of plate formers
  - Thin 3.3 mm vs Thick 6.3 mm
  - Thin plate => thinner film
  - Thin plate => darker color
    (same curing conditions)

- Conclusion
  - Plates differ in heat capacity.
  - Curing conditions for production setting may vary (glove formers).
  - Thick formers for later studies.
Result 3
Added water

- Water added to Bi₂O₃ powder - avoid coagulating latex
  - 18 phr to 50 phr tested
  - More water => Dotted film surface
  - More water => Lighter color (same curing condition)
  - Impact on film thickness noticed but not statistically significant

- Conclusion
  - Lower compound viscosity and more time to evaporate water, allowing Bi₂O₃ to sediment before crosslink happens.
  - Added water should be kept constant and as low as possible, only to moisten the filler
  - 18 phr used for later studies
Result 4

Tensile performance

All data \((n = 84)\)
- Sulfur: 2.5 - 3.4 phr
- \(Bi_2O_3\): 120 - 150 phr

Of all 84 samples
- 79 passed ASTM D3578 examination glove standard.
- 22 passed ASTM D3577 surgical glove standard(*)

Tensile properties (Mean ± SD)
- Tensile strength: 22.8 ± 3.5 MPa
- Ultimate elongation: 765.8% ± 36.5%
- Modulus (at 500%): 3.69 ± 0.82 MPa
Compound formulation
Modulus

All data (n = 84)
Sulfur 2.5 - 3.4 phr
Bi$_2$O$_3$ 120 - 150 phr

<table>
<thead>
<tr>
<th>Modulus at 500% (MPa)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>2.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25% Percentile</td>
<td>2.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>3.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75% Percentile</td>
<td>4.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>5.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>3.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std. Deviation</td>
<td>0.82</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Bar chart showing modulus values](chart.png)

- Inversely affected by sulfur loading (p<0.01).
- Effect of Bi$_2$O$_3$ not significant.
- All passed both standards.
Inversely affected by sulfur loading ($p<0.01$).

Effect of Bi$_2$O$_3$ not significant.

All passed exam glove standard (higher is better).

54 passed surgical glove standard.
Negatively affected by Bi$_2$O$_3$ loading (p<0.01).
Positively affected by sulfur loading (p<0.01).
79 passed exam glove standard (5 failed at 2.5 S + 150 Bi$_2$O$_3$).
33 passed surgical glove standard (high sulfur + baseline bismuth).
Summary

Compound Formulation

• Sulfur
  • Reduces softness and elongation, increases strength
  • 3.2 phr sulfur - sweet spot

• Examination glove performance
  • Consistently achieved except low sulfur + high $\text{Bi}_2\text{O}_3$
  • Tolerant to varied curing conditions

• Surgical glove performance
  • Consistently achieved only with high sulfur + 120 phr $\text{Bi}_2\text{O}_3$
  • Tolerant to varied curing conditions
  • Some at high sulfur + 150 phr $\text{Bi}_2\text{O}_3$

• Optimization target
  • Surgical glove performance + 150 phr $\text{Bi}_2\text{O}_3$
  • Determine optimal curing conditions
Optimal curing temperature

All data (n = 84)

Sulfur 2.5 - 3.4 phr

$Bi_2O_3$ 120 - 150 phr

- Best curing temperature varies, but 90 °C works more consistently across formulation variants.
Optimal temperature x time

Filtered data ($n = 20$)

Sulfur 3.4 phr
$Bi_2O_3$ 150 phr

- Optimal curing condition is 60 – 75 min at 90 °C
Regression Analysis

• Multivariate linear regression to build prediction models for the tensile properties. Guide future R&D.

Evaluated factors

• Sulfur and Bi$_2$O$_3$ loading.
• Film thickness was used as factor instead of response, replacing added water and former differences.
• Curing temperature and time are known to affect filler free GNR film tensile properties in a nonlinear pattern. They were transformed and combined as one.

Criteria

• Factors with p-values $\geq 0.05$ were discarded.
• Factors with unreasonable causalities were removed (e.g. Bi$_2$O$_3$ loading reduces modulus – likely overriding effect of sulfur loading).
Regression Analysis
Modulus

(modulus at 500% strain)
= −3.3 + 1.2 × (sulfur phr) + 0.18 × Ln(cure temp) × Ln(cure time)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>S.E.</th>
<th>t Stat</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-3.275</td>
<td>1.153</td>
<td>-2.841</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.186</td>
<td>0.176</td>
<td>6.747</td>
</tr>
<tr>
<td>Ln(c.temp)xLn(c.time)</td>
<td>0.180</td>
<td>0.065</td>
<td>2.772</td>
</tr>
</tbody>
</table>

- Increases with sulfur loading.
- Affected by curing conditions.
Regression Analysis
Ultimate Elongation

\[(\text{ultimate elongation}) = 7.46 + 6.79 \times (\text{thickness}) - 0.096 \times \ln(\text{cure temp}) \times \ln(\text{cure time})\]

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>S.E.</th>
<th>t Stat</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>7.460</td>
<td>1.027</td>
<td>7.266 &lt;0.0001</td>
</tr>
<tr>
<td>Thickness</td>
<td>6.790</td>
<td>2.693</td>
<td>2.522 &lt;0.05</td>
</tr>
<tr>
<td>Ln(c.temp)xLn(c.time)</td>
<td>-0.096</td>
<td>0.035</td>
<td>-2.756 &lt;0.01</td>
</tr>
</tbody>
</table>

- Should be slightly affected by sulfur loading, but wasn’t detected.
- Determined by constant term.
- Affected by curing conditions.
- **Increases with film thickness.**
Regression Analysis

Tensile strength

\[
(\text{ultimate elongation}) = 7.46 + 6.79 \times (\text{thickness}) - 0.096 \times \ln(\text{cure temp}) \times \ln(\text{cure time})
\]

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>S.E.</th>
<th>t Stat</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>15.554</td>
<td>5.641</td>
<td>2.757</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3.743</td>
<td>0.659</td>
<td>5.681</td>
</tr>
<tr>
<td>Bi(_2)O(_3)</td>
<td>-0.113</td>
<td>0.019</td>
<td>-5.962</td>
</tr>
<tr>
<td>Ln(\text{c.temp})xLn(\text{c.time})</td>
<td>0.638</td>
<td>0.223</td>
<td>2.862</td>
</tr>
</tbody>
</table>

- Increases with sulfur loading.
- Decreases with Bi\(_2\)O\(_3\) loading.
- Affected by curing conditions.
Predicted Tensile
Based on regression

<table>
<thead>
<tr>
<th></th>
<th>Surgical RA glove</th>
<th></th>
<th>Exam RA glove</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>Sulfur (phr)</td>
<td>3.2</td>
<td>3.3</td>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Bi$_2$O$_3$ (phr)</td>
<td>120</td>
<td>140</td>
<td>140</td>
<td>150</td>
</tr>
<tr>
<td>Cure temp (°C)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Cure time (min)</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>0.28</td>
<td>0.28</td>
<td>0.30</td>
<td>0.28</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>26.20</td>
<td>24.32</td>
<td>24.69</td>
<td>22.81</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>752</td>
<td>752</td>
<td>766</td>
<td>752</td>
</tr>
<tr>
<td>Modulus (MPa)</td>
<td>3.98</td>
<td>4.10</td>
<td>4.22</td>
<td>3.98</td>
</tr>
<tr>
<td>Estimated attenuation (% to ASTM baseline)*</td>
<td>100</td>
<td>117</td>
<td><strong>125</strong></td>
<td>125</td>
</tr>
</tbody>
</table>

* (attenuation % to baseline)=$(Bi_2O_3 \text{ phr})/120*(\text{thickness})/0.28
Conclusion

• Using GNR latex, medical grade RA gloves are achievable.
  • Formulation
    • Sulfur affects all tensile properties, best 3.2 phr.
    • Bi$_2$O$_3$ reduces tensile strength, 120 phr - 200 phr.
  • Curing conditions
    • Critical for higher filler loading + surgical glove performance.
    • Optimal 90 °C, 60 to 75 min (film samples).
    • Optimization needed for commercial production, esp. for higher filler loading surgical RA gloves (differences in production settings from lab).

• Can be made into other radiation protective garments.
  • Radiation shielding thyroid shield, radiation shielding apron
Significance

- GNRL - a specialty latex with distinct properties
  - High elongation, low modulus, comparable strength
  - Circumallergenic (extremely low protein & no *Hevea* proteins)
  - Cryo-malleability

- New product development and market growth points
  - Ultrathin and super soft latex products
  - Softer lineman’s gloves
  - High altitude weather balloons (more payload, ascend faster)
  - Low temperature applications
Thank You!

Questions?