Influence of modified bio-oils on the fracture mechanics behavior of SBR polymers

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MOTIVATION

Failure of polymers

Improvement of Resistance against Crack initiation and propagation

- Stretching
- Weathering / Long time application
- Continuous bending
- Compression
- Low crack initiation/propagation energy

http://www.therangerstation.com/tech_library/buying_used_tires.shtml
Oils → Plasticizers

Organic compound, reducing entanglements of polymer chain, internal friction and viscosity

**Source of plasticizers**

- **Non-renewable**: Mineral oil (Paraffinic, naphthenic, aromatic oil)
- **Renewable**: Vegetable oil (bio-oil), modified vegetable oil
- **Synthetic**: Phthalates, Polymeric plasticizers

**Influence on polymer**

- Flexibility
- Workability
- Distensibility

**Conditions**

- Non-toxic
- Better compatibility
- Good aging behavior
- No discoloration
- No interaction
- Non-volatile
Why bio-oils?

biological resource; eco-friendly; renewable; sustainable*

*Recent works investigate mechanical properties....

**Results:** Positive (Some selected modified bio-oils)

Pechurai (2015) **castor oil and jatropha oil with SBR.**
Bio-oils enhanced the mechanical properties of SBR.

Wang (2016) **palm oil with EPDM.**
Plam oil loaded EPDM increased some selected mechanical properties.

Petrovic (2017) **polymerized soybean oil with EPDM.**
This modified bio-oils increased some selected mechanical properties.

S. Kumar (2019) **epoxidized soybean oil and castor oil with PVC**
Bio-oils were compatible and enhanced mechanical and thermal properties
Bio-oils used to enhance mechanical properties in last two decades

✓ Rice bran oil/epoxidized rice bran oil (2003)
✓ Coconut oil (2007)
✓ Castor oil (2007)
✓ Rubber seed oil (2008)
✓ Epoxidized soybean oil (2013)
✓ Linseed oil (2015)
✓ Orange oil (2015)
✓ Epoxidized soybean oil/castor oil (2019)

Inspired to enhance the fracture mechanics behavior

Investigation of the compatibility between bio-oil and SBR upon fracture behavior as well as mechanical and physical behavior
INTRODUCTION

Fracture mechanics

Driving energy on a crack to characterize the material’s resistance to fracture

Type of loading to investigate:

- Static loading: Stress remains same
- Quasi-static loading: Slowly increasing stress
- Impact loading: Sudden increasing stress
- Cyclic loading: Dynamic changing

Stress

Time

Stress

Time

Stress

Time

Stress

Time

10^{-3} \text{ to } 1000 \text{ mm/min}

1 \text{ to } 80 \text{ m/sec}

Quasi-static fracture mechanics test

Instrumented tensile impact test (ITIT)

Stable crack propagation energy

Unstable crack propagation energy

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Crack propagation and fracture mechanics concepts

Unstable crack propagation

Linear-Elastic Fracture Mechanics (LEFM)

Stable crack propagation

Yielding Fracture Mechanics (YFM)

Transition region unstable/stable crack propagation

Stress intensity factor ($K$)

$\delta, J$-Integral

Crack opening ($I_R$)

Stable crack propagation energy ($T_{J^*}$)

Fracture toughness measurements in Engineering plastics, Wolfgang Grellmann and Sabine Seider; Polymer testing, 2013

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### EXPERIMENTAL: Recipe

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Details</th>
<th>Amount (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>SPRINTAN™ SLR 4602/4630</td>
<td>100</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>TDAE/EECO 0/12.5/25/37.5</td>
<td></td>
</tr>
<tr>
<td>Carbon-black</td>
<td>Filler CORAX® N220</td>
<td>40</td>
</tr>
<tr>
<td>**6PPD</td>
<td>Antioxidant</td>
<td>1.5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>Processing aids</td>
<td>1</td>
</tr>
<tr>
<td>ZnO</td>
<td>Activator</td>
<td>3</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Crosslinking agent</td>
<td>1.75</td>
</tr>
<tr>
<td>***CBS</td>
<td>Accelerator</td>
<td>1.05</td>
</tr>
</tbody>
</table>

**Non-renewable oil (Conventional plasticizer)**
- Treated distillate aromatic extract
- TDAE
- M.W. ~180 g mol⁻¹

**Modified bio-oil**
- Epoxidized ester glycerol formal from canola oil
- EECO
- M.W. ~400 g mol⁻¹

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EXPERIMENTAL: Materials

Styrene-butadiene rubber (SBR)

Application


https://www.achilles-reifen.de/de/

Block copolymer

1,4 Butadiene

Vinyl- butadiene

Styrene

[SPRINTAN™](Schkopau) SLR 4602 SLR 4630

<table>
<thead>
<tr>
<th>Name</th>
<th>S-21</th>
<th>S-25T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (MU)</td>
<td>65</td>
<td>55</td>
</tr>
<tr>
<td>Styrene (%)</td>
<td>21</td>
<td>25</td>
</tr>
<tr>
<td>Vinyl (%)</td>
<td>62</td>
<td>62</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>-25</td>
<td>-28</td>
</tr>
<tr>
<td>TDAE (phr)</td>
<td>-</td>
<td>37.5</td>
</tr>
</tbody>
</table>

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Mechanical and physical properties

**Mechanical tests:**
- Hardness (Shore A); DIN ISO 7619-1
- Tear resistance test; DIN ISO 34-1

**Analytic:**
- DMA

**Physical test:**
- ✔️ Oil migration test; Press method

**Fracture mechanic tests:**
- ✔️ Quasi-static fracture mechanics test
- ✔️ Instrumented tensile impact test

**Aging properties**
Reference 0 day
Aged for 3, 15 and 30 days at 80°C in hot air oven
Oil migration test

Press method

60 °C

Measure the mass after a time period
Quasi-static fracture mechanics test (in-situ test)

Single specimen method (SSM)
Crosshead speed 50 mm/min

Crack resistance value ($J$)

$$J = \frac{\eta A}{B(W - \alpha)}$$

- $A$: energy
- $B$: specimen thickness
- $W$: specimen width
- $\alpha$: initial notch size
- $\eta$: geometry function (~1)

Crack initiation energy ($J_i$)

Stable crack propagation energy ($T_J^*$)

Fracture toughness measurements in Engineering plastics, Wolfgang Grellmann and Sabine Seider; Polymer testing, 2013
Instrumented tensile impact test (ITIT)

Unstable crack propagation energy ($J_d$)

$$J_d = \frac{\eta A_{\text{max}}}{B(W - a)}$$

$$\eta = -0.06 + 5.99 \left(\frac{a}{W}\right) - 7.42 \left(\frac{a}{W}\right)^2 + 3.29 \left(\frac{a}{W}\right)^3$$

Pendulum device
Impact energy: 7.5 J
Falling angle: 150°
Speed: 3.7 m/sec

Double-edged notch tension (DENT) specimen

Top view
Side view
Influence of plasticizer type on mechanical and physical behavior

- **Hardness**
- **Tear resistance**
- **Glass transition temperature**
- **Migration properties**

37.5 phr plasticizer 40 phr CB

TDAE: M.W ~180 g mol\(^{-1}\)
EECO: M.W ~400 g mol\(^{-1}\)

15 days at 60 °C
Influence of plasticizer concentration on the resistance against crack initiation and stable crack propagation

![Graph showing the influence of plasticizer concentration on crack resistance](image)

Quasi-static fracture mechanics test

** SENT Specimens **

** S-21/TDAE **
- Without oil
- 12.5 phr
- 25 phr
- 37.5 phr
- S-25T

** S-21/EECO **
- Without oil
- 12.5 phr
- 25 phr
- 37.5 phr
- S-25T

** M. Rahman / Influence of modified bio-oils on the fracture mechanics behavior of SBR polymers **
Influence of plasticizer type on the resistance against crack initiation and stable crack propagation

Quasi-static fracture mechanics test
Influence of plasticizer type and concentration on the resistance against unstable crack propagation

Instrumented tensile impact test (ITIT)
Influence of thermo-oxidative aging at 80 °C on the fracture mechanics behavior

Quasi-static fracture mechanics test

Instrumented tensile impact test (ITIT)
Finally, come back to the starting point and highlight the benefits of modified bio-oil as plasticizer!
Thank you for your attention

Acknowledgment

We would like to acknowledge the GLACON CHEMIE for supplying the bio-oils and TRINSEO for SBR samples.