Silane-crosslinking efficiency in wood-polyethylene composites: Study of different polyethylenes

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Background
Challenges for WPCs

- Strength and toughness
- Lowering the weight
- Improving long-term material properties
Challenges for WPCs

- Strength and toughness
- Lowering the weight
- Improving long-term material properties

Crosslinking:

- Higher strength and toughness
- Creep resistance
Crosslinked WPCs

Non-crosslinked

Crosslinked

Polymer matrix

WF
Crosslinked WPCs

Non-crosslinked

Crosslinked

Polymer matrix

Creep resistance
Crosslinked WPCs

Non-crosslinked

Crosslinked

Strength and toughness

Polymer matrix
Previous studies

**Pre-treated wood flour/fibers**
Sapieha et al. (1990), Kuan et al. (2004), Xiong et al. (2008), etc.

**Add reactants during compounding**
Nogelova et al. (1998), Janigova et al. (2001), Bengtsson et al. (2006)
Previous studies

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Peroxide-crosslinking
Silane-crosslinking
Crosslinked polyethylene

Peroxide-crosslinking

PE
Crosslinked polyethylene

Peroxide-crosslinking

\[ \text{PE} \rightarrow \text{Crosslinked PE} \]

Silane-crosslinking

\[
\begin{align*}
\text{MeO} & \quad \text{Si} & \quad \text{OMe} \\
\text{OMe} & \quad +3 \text{H}_2\text{O} & \quad \text{OH} \\
\text{HO} & \quad \text{Si} & \quad \text{OH} \\
& & +3 \text{CH}_3\text{OH}
\end{align*}
\]
Crosslinked polyethylene

Peroxiide-crosslinking

Silane-crosslinking

\[
\text{PE} \quad \rightarrow \quad \text{MeO}_2\text{Si} \quad \rightarrow \quad \text{HO}_2\text{Si} \quad + 3 \text{H}_2\text{O}
\]

\[
\rightarrow \quad \text{HO}_3\text{Si} \quad + 3 \text{CH}_3\text{OH}
\]

\[
\rightarrow \quad \text{HO}_2\text{Si} \quad + \text{H}_2\text{O}
\]
Crosslinked polyethylene

Peroxide-crosslinking

Silane-crosslinking

Molten state

Solid state
Crosslinked polyethylene

Peroxide-crosslinking

Silane-crosslinking

Side-reaction (Scorch)

Molten state

Solid state
Silane-crosslinked polyethylene

Differences between type of polyethylene

High-density polyethylene
**HDPE**

- Less
- Less
- Slower

Low-density polyethylene
**LDPE**

- More
- More
- Faster

Polymer chain scission
Scorch
Curing

Silane crosslinked WPC

One-step process:
(Bengtsson et al., 2006)
Silane crosslinked WPC

One-step process:
(Bengtsson et al., 2006)

Compounding
Silane-grafting
Profiling

Store composite

H₂O
Objective for the study

- Investigate possibility to use silane-technology for LDPE-WPCs
- Compare results to our previous study of crosslinked HDPE-WPC
Materials and Processing
Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE MFI 12</td>
<td>47 wt-%</td>
</tr>
<tr>
<td>LDPE MFI 0.4</td>
<td>50 wt-%</td>
</tr>
<tr>
<td>Wood flour</td>
<td>3 wt-%</td>
</tr>
<tr>
<td>TPW113 (Struktol, U.S.A.)</td>
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- **Wood flour**: Softwood, 300-500μm
- **Lubricant**: TPW113 (Struktol, U.S.A.)
Materials

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>LDPE (recycled)</th>
<th>Lubricant</th>
<th>Solution</th>
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<td>DCP 98% (Sigma Aldrich, Japan)</td>
<td>25:1 w/w</td>
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Reactive extrusion

Twin screw extrusion
- Compounding and profiling
  - Throughput 5.2 kg/h
  - Residence time 55-60 s.
  - Melt temp. ~195°C

(Coperion W&P ZSK18 MEGAlab)
Curing conditions

**Room temperature (RT)**
- 21°C
- RH 30-40%

**Sauna (SA)**
- 90°C
- RH close to 100%

**Storing times:**
- 0, 3, 6, 12 hours,
- 1, 2, 3, 4, 6, 9 days
Sample coding

**HDPE-composites**
- HD Non-X
- HD-X

**LDPE-composites**
- LD Non-X
- LD-X
- LD-X (low)
Testing and Results
Processing

HDPE-composite

LDPE-composite

Non HD-X Non LD-X LD-X (low)
Processing

**Extruder torque:**

- **HDPE-composite**
  - Non: 35%
  - HD-X: 60%

- **LDPE-composite**
  - Non: 45%
  - LD-X (low): 60%
  - LD-X: 70%
**Processing**

**HDPE-composite**
- Extruder torque: 35% 60%
- Die swelling: Not significant

**LDPE-composite**
- Extruder torque: 45% 60-70%
- Die swelling: 4% 20% 40%
Degree of crosslinking

Measure insoluble gel content
(ASTM D2765)

- Sample in 120 Mesh pouch
- In boiling xylene for 12 hours
- Extracted mass (%) measured
- Degree of crosslinking = 100 – Extract (%)
Degree of crosslinking

HD-X

LD-X

Storing time (days)

0 1 2 3 4 5 6 7 8 9

0% 20% 40% 60% 80% 100%

56%

35%

Storing time (days)

0 1 2 3 4 5 6 7 8 9

0% 20% 40% 60% 80% 100%
Degree of crosslinking

**HD-X**
- RT: 35%
- SA: 60%

**LD-X (Low)**
- RT: 39%
- SA: 56%
Mechanical testing

LDPE-composites
Flexural properties

HDPE-composites*
Tensile properties

* Grubbström and Oksman 2009
Mechanical properties

HDPE-composites

- Tensile stress (MPa)
- Strain (%)

Graph showing tensile stress vs. strain for HD-X and Non-X materials at RT and SA conditions.
Mechanical properties

LDPE-composites

Flexural stress (MPa) vs. Strain (%)

- Non-X
- LD-X (low)
- LD-X

RT
SA
Morphology

HDPE-Composite

LDPE-Composite

Non-X

Crosslinked
Short-term creep

**DMA**
(TA Instruments)

- **Specimen**: 60.0 x 12.5 x 2.5 (mm)
- **Dual cantilever mode**
- **Static stress 5 MPa**
- **30°C**
- **5 hours + 1 hour recovery**
Short-term creep

**HDPE-composites**

- RT
- SA

**LDPE-composites**

- LD-X
- Non-X
- LD-X (low)
Conclusions
Conclusions

- There are differences in crosslinking efficiency depending on type of polyethylene in the WPC
- The technology works for both HDPE and LDPE
- LDPE-composite:
  - More sensitive for reactants
  - Cures faster
  - Do not need storing in Sauna
Future work

- Minimize crosslinking in extrusion process
- Silane-crosslinking process: RT, SA
- Long-term properties
Acknowledgements

- Skellefteå Kraft and Nordea for financial support
Questions?
<table>
<thead>
<tr>
<th>Sample code</th>
<th>$\sigma$ (MPa)</th>
<th>$E$ (MPa)</th>
<th>$\varepsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat LDPE$^a$</td>
<td>18 ± 1</td>
<td>260 ± 40</td>
<td>14,4 ± 0,4</td>
</tr>
<tr>
<td>LD Non-X</td>
<td>13 ± 1</td>
<td>1768 ± 163</td>
<td>2,6 ± 0,3</td>
</tr>
<tr>
<td>LD-X RT</td>
<td>16 ± 1</td>
<td>675 ± 70</td>
<td>7,6 ± 0,3</td>
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<tr>
<td>LD-X SA</td>
<td>14 ± 1</td>
<td>646 ± 60</td>
<td>6,1 ± 0,9</td>
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<tr>
<td>LD-X RT (low)</td>
<td>26 ± 2</td>
<td>1423 ± 160</td>
<td>5,1 ± 0,5</td>
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<tr>
<td>LD-X SA (low)</td>
<td>24 ± 1</td>
<td>1382 ± 70</td>
<td>4,7 ± 0,3</td>
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<tr>
<td>Neat HDPE$^b$</td>
<td>26 ± 1</td>
<td>1266 ± 64</td>
<td>6,1 ± 0,4</td>
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<tr>
<td>HD Non-X</td>
<td>11 ± 2</td>
<td>1562 ± 204</td>
<td>1,8 ± 0,3</td>
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<tr>
<td>HD-X RT</td>
<td>18 ± 1</td>
<td>1749 ± 97</td>
<td>2,4 ± 0,1</td>
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<tr>
<td>HD-X SA</td>
<td>19 ± 2</td>
<td>1888 ± 118</td>
<td>2,2 ± 0,2</td>
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</table>

$^a$ Flexural properties for all HDPE-samples

$^b$ Tensile properties for all LDPE-samples
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<th>Storing mode</th>
<th>Storing time</th>
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<tbody>
<tr>
<td></td>
<td>0 hour</td>
<td>3 hours</td>
</tr>
<tr>
<td>LD-X</td>
<td>Sauna</td>
<td>56%</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>56%</td>
</tr>
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<td>Sauna</td>
<td>35%</td>
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