Reactive Modification of Engineering Thermoplastics

CHALLENGES IN EXTRUSION OF POLYMERS, Leoben, 11.06.2014
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• Example Polyamides + Polyolefins
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Developement

• 2002 - 2005
  – Office for engineering services in Leoben
  – 2002-2004 in a Start-Up Center (ZAT)

• From 2005
  – Removal to Niklasdorf
  – Starting up of the Compounding Line
Our Topics

• Formulation and Testing of Recipes and their Production in Compounding Processes

• Development of Compounding Strategies

• Consulting of Customers (mainly polymer processing and polymer producing industries)
What we offer

- Selection of Raw materials
- Fundamental Research
- Formulation
- Compounding of the Product

Customer

Manufacturers

Specification

Fundamental Research

External Research
Scope

Initial Situation – Needs of Processing Industries

Injection Moulding

- Impact Load or Shock Absorbance
- Constant mechanical properties over a broad range of temperature
- Compatibility between different polymers

Extrusion

- Increasing of melt strength
- Compatibility between different polymers
- Adhesion between layers in co extrusion
### Scope

**Commercial Impact Modification vs. Heat Resistance**

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Polymer</th>
<th>Density in g/cm³</th>
<th>Notched Impact Str. kJ/m² at T=-30°C</th>
<th>HDT A in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stanyl TW 341</td>
<td>PA46</td>
<td>1,18</td>
<td>4</td>
<td>190</td>
</tr>
<tr>
<td>Stanyl TW 363</td>
<td>PA 46 impact mod.</td>
<td>1,1</td>
<td>30</td>
<td>90</td>
</tr>
</tbody>
</table>

Semicrystalline, linear Engineering Thermoplastics + Branched/Crosslinked Reactive Impact Modifier
Strategy
Combining of Thermomechanic Properties

Shear Modulus vs. Temperature

$T_g \gg$ Working Temperature

$T_g \ll$ Working Temperature

Cross Linking Density

High

Low

$G'$

$log G'$

$log \tan \delta$

$T_N$ $T_g$ $T_\alpha$ $T_S$ $T_f$ $T$

$T_N$ $T_g$ $T$
Selection of Polymer Partners
Targets and Criterias

• Targets for the Resulting Polymer Matrix
  – Covalent bonded Impact Modifier
    • Maleic Anhydrid for Polyamides
    • Acrylates for Polyesters
  – Interchain-Block-Copolymer
  – Intrinsic Compatibilizer/Coupling Agent

• Selection Criteria for Impact Modifiers
  – Tg far below working temperature
  – Processing Temperature Stability
  – Moderate Functionality

Processing of a Functionalised Impact Modifier

Reactions

Functionalising by Graft-Copolimerisation

Desired Pathway
Analysis of a Functionalised Impact Modifier

*Determination of the Graft Level*

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**Graphical Analysis**

- **Wellenzahl**
  - 4000 cm\(^{-1}\)
  - 3000 cm\(^{-1}\)
  - 2000 cm\(^{-1}\)
  - 1000 cm\(^{-1}\)

- **Maleic Acid**
  - 1710 cm\(^{-1}\)
- **Maleic Anhydride**
  - 1786 cm\(^{-1}\)

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**wt.%**

- 0.0
- 0.1
- 0.2
- 0.3
- 0.4
- 0.5
- 0.6

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**Gehalt an Pfropfmonomer - Ist**

- PE1
- PE2

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**Gehalt an Pfropfmonomer - Soll**

- 0.0
- 0.1
- 0.2
- 0.3
- 0.4
- 0.5
- 0.6
Analysis of a Functionalised Impact Modifier

Determination of Side Reaction (Degradation)

Determination of Degradation

Reduction of the torque in an Internal Mixer
Reactive Compounding
Pro’s und Con’s

- **Pro’s**
  - Lower density, similar heat resistance
  - Higher melt strength - caused by long chain branching and/or crosslinking
  - Improved Hydrolysis Stability
  - Mechanical properties can be designed over a huge range
  - Improvement of the surface quality of glass fibre reinforced formulations

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Modification</th>
<th>Density in g/cm³</th>
<th>HDT A in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA 46 Stanyl TW 300</td>
<td>Base Resin</td>
<td>1.18</td>
<td>170</td>
</tr>
<tr>
<td>APC PA 46 mod.</td>
<td>Interchain Copolymer</td>
<td>1.10</td>
<td>166</td>
</tr>
<tr>
<td>PA 46 Stanyl TW 363</td>
<td>Non Reactive Impact Modified Blend</td>
<td>1.10</td>
<td>90</td>
</tr>
</tbody>
</table>

- **Con’s**
  - Flowability
  - Could be difficult to add further additives
Example: Fire Fighting Helmet

**Technical Requirements**

- **Thermal Requirements**
  - No Dripping or Delamination at $T = 250 \, ^\circ C$
  - No Self Ignition at $T = 250 \, ^\circ C$
  - Burning shorter than 5 s after flame treatment at $1000 \, ^\circ C$ for 10 s

- **Mechanical Stability at $T = 250 \, ^\circ C$ and at $T = -50$**
  - A sphere with 5 kg mass drops down from 2,5 m height.
  - A sharply edged dart with a mass of 1 kg hits from a height of 2,5 m the helmet and must not destroy the exterior shell.
  - At a load of 630 N the deformation should not exceed 40 mm, the remaining deformation must not exceed 15 mm

- **Chemical Stability**
  Against: $H_2SO_4$ (30 %), NaOH (10 %), p-Xylol, Butanol
Example: Shell of Skiing Boot

Requirements

Material
- Low $T_G (< -50 \, ^\circ\text{C})$
- Low changes of modulus $-30 \, ^\circ\text{C}$ to $20 \, ^\circ\text{C}$
- High Elasticity
- Shock Absorbance
- UV-Stability
- Fracture Toughness
- Stability against water
- Low temperature flex
- Strength against Abrasion

Economics
- Product costs
- Low loss through waste

Processing
- Injection Moulding
- Combine with other materials
- Surface Quality
Example Shell of Skiing Boot

Results

Racing

New generation of Skiing Boots

World Cup Winner MEN 2011

Fischer VacuumFit®
Reactive Compounding
Spectra of Properties and Applications

Polyamid 66
PA 46 LGF 45 Impact Modified
PA 6 Impact Modified

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>PA 46 LGF 45 Impact Modified</th>
<th>Polyamid 66</th>
<th>PA 6 Impact Modified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Modulus</td>
<td>MPa</td>
<td>13.000</td>
<td>3.000</td>
<td>200-300</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>MPa</td>
<td>210</td>
<td>85</td>
<td>25</td>
</tr>
<tr>
<td>Elongation at Break</td>
<td>%</td>
<td>2</td>
<td>25</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>Heat Distortion Temperature</td>
<td>HDT A °C</td>
<td>&gt; 250 °C</td>
<td>75</td>
<td>45</td>
</tr>
<tr>
<td>Application</td>
<td></td>
<td>Shell Fire Fighting Helmet</td>
<td>Bearings, Connectors</td>
<td>Shell Skiing Boots</td>
</tr>
</tbody>
</table>
Development

Coextrusion of PA´s for Building Applications

Requirements

– Excellent Adhesion to Different Materials
– Compatibility of different layers
– Long Term UV-Stability
– Weldable
– Temperature Stability up to 80 °C
– Flexibility for Installation
Development Improvement of Barrier Properties
PET/PE-Sheets

MATERIAL
• Recycled PET (Bottle Grades)
• Blended with 50% PE

APPLICATION
• Coated Papers for Packaging
Advanced Polymer Compounds

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