Copolymers, composites and crystallization: Working with DPI for tomorrow’s polyolefins

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Borealis – Who we are

• More than 40 years of heritage in polyolefins
• State-of-the-art bimodal Borstar®
  PE & PP technology
• Over 55 new product launches in 2005
• EUR 6 billion revenue in sales
• 4,500 employees in 11 countries
• Four European hubs
• Expanding in Middle East and Asia
Content

• Polymer development is teamwork!
• Three examples for working with DPI:
  • Polyolefin copolymers with well-defined architecture
  • Revolutionary ways towards polymer nanocomposites
  • Understanding fundamentals of crystallization
• Stepping into the 21st century
Polymer development is teamwork!

- Reactivity / stability
- Polymer chain & morphology
- Chain structure control
- Post-reactor modification
- Catalyst chemistry
- Characterization techniques
- Particle formation
- Processing & structure formation
- Reactor design
- New conversion processes
- Mechanics & Long-term stability
- Economic performance
Orders of Magnitude, ...

- Molecules & Crystal lattices: 100 pm
- Lamellae & Nanoparticles: 10 nm
- Multiphase Structures: 1 µm
- Spherulites & Fillers: 100 µm
- Superstructures & Defects: 1 mm
- Others: 10 mm
... Steps of Production
Borstar® PP as example for a “holistic view”

Catalysis

Polymerisation

Extrusion

Catalyst

Gas phase reactor

Loop reactor

Gas phase reactor

Additives, Fillers etc.

Peroxide, Monomer

Product

Propylene

Comonomer

Hydrogen

Molecule design

Composition design

Property design

Tailored reactor materials
Polyolefin copolymers with well-defined architecture

- Di- and triblock copolymers are ideal compatibilizers – but so far not accessible for polyolefins
- New development in DPI – iPP-EPR(-iPP) as well as iPP-PE(-iPP) etc. di- and triblocks accessible from phenoxyimine catalyst
- Living polymerization allows excellent structure & molecular weight control
- Question of phase structure and performance in polyolefin blends (PP/PE, PP/EPR, …)
Morphology of di- and triblock systems
PP/PE blends with different compatibilisers - Morphology

![Graph showing PSD average/µm and G' (+23°C)/MPa for different PP/PE blends with compatibilisers.](image)

- PP_LLDPE
- PP_LLDPE_Versify
- PP_LLDPE_EPR
- PP_LLDPE_DIBLOCK
- PP_LLDPE_TRIBLOCK

 PSD average/µm:
- 200 nm

G' (+23°C)/MPa:
- 600
- 620
- 640
- 660
- 680
- 700
- 720
- 740
- 760
- 780
- 800
- 820
Triblock action in PP/EPR blends
Patent application filed ...

• „Compatibilized polyolefin compositions” – EP 07115376.1 (DPI NoPOComp, ID 07.008) filed August 31st 2007

• Combination of iPP with different polyolefin & di/triblock protected

• Morphology-related toughness enhancement demonstrated

• Very efficient at low molecular weight – better processability
... next steps to be decided

- Development may be relevant for a number of areas
- Soft/elastic polyolefins with good sterilisation resistance among targets
- Possibilities for scale-up to be checked (catalyst, process, particle formation, …)
Revolutionary ways towards polymer nanocomposites

• Dispersion is the predominant problem in PO nanocomposites …

PP-Homo
+ 7% Organoclay (Südchemie)
+ 7% PP-g-MAH (Crompton)

PA-6
+ 7% Organoclay (Südchemie)

• … effectively hindering commercialization & success!
In-situ pathways to PO Nanocomposites

• … from the **Nanofiller**: Polymerization around well-dispersed nanoparticles (PA-6 – polycondensation, PO – catalytic, …)

• … from the **Polymer**: Adsorption of a precursor to polymer powder followed by particle formation (e.g. hydrolysis of silane)
New approach to processability improvement

- Lab-scale development
  - In-situ preparation of mesoporous silica nanoparticles (MPNPs) by silane sorption & decomposition
  - Massive viscosity reduction at 2,000-8,000 ppm silica level, mechanics equal or improved
- Patent application filed – EP 05101388.6
- Two lines of development
  - Scale-up & application testing – Borealis
  - Scientific understanding and extension to other polymers - TUE
First Scale-Up Results

- In-situ generation with TEOS adsorption and hydrolysis (kg-scale)
- Viscosity reduction in concentration range 0.1-0.5 wt% silica
- Both stiffness & impact slightly improved
- Different results with Aerosil compounds

![Characterisation of polymer-melts by dynamic measurements](image)

Temp.: 200°C

Characterisation of polymer-melts by dynamic measurements

- SR 2000
- TP49305-1
- TP49305-2
- TP49305-3
- TP49305-4

Viscosity $\eta^*$ vs. angular frequency $\omega$ at 200°C

- Base
- 0.2% MPNP
- 0.5% MPNP
- 1.2% MPNP
... but problems in further scale-up

- PP powder morphology has dominant influence on formation of suitable nanoparticles
- Change in surface/volume ratio makes hydrolysis increasingly difficult
- Better understanding of viscosity reduction required for success
Understanding fundamentals of crystallization

• Practically achieved mechanical performance of both PP and PE is far below technical limits
• New polymers often fail because of processing troubles (e.g. SSC-PO)

Figure 1.10 Scales showing tensile strength and modulus for polyethylene. (Reproduced from Barham, P. J.; Keller, A. J. Mat. Sci. 1985, 20, 2281).
Processing effects – Rheology & crystallisation

- Molecular structure
- Additives (Nucleants)
- Processing parameters
- Phase structure
- Rheology
- Crystalline structure
Models, Parameters & Targets

To be widely applicable, a crystallization model must:

• ... be compatible with existing CAE(D) software
• ... have a limited number of parameters with possible correlation to structural features of the polymer
• ... be capable of predicting mechanics and dimensional stability
From molecules to crystals

**Strong flow**

**Little or no flow**

Spherulite

Shish-kebab

Skin

Core
Understanding materials ...

Example: Polymer/nucleation interaction

• Similarities in high molecular weight & nucleant effects on flow-induced crystallization
• Enables process-related material design
... and understanding processes

Example: \( pVT \) setup

- Allows rapid characterization of a semicrystalline polymer in wide range of solidification conditions
- Can deliver parameters for tomorrow’s processing simulations
- Could become standard equipment for processing laboratories
Next steps: From PP to PE
PE: a similar picture … chain regularity & MWD effects

Shish-kebab structures in bimodal LLDPE

Density effects on quiescent crystallization of HDPE / LLDPE
Stepping into the 21\textsuperscript{st} century

\textbf{The vision:}

- Interdisciplinary university education is standard
- Industrial and academic research are complementary
- Nanotechnology has become efficient & economic
- Sustainability is becoming reality
- Polyolefins are widely accepted performance materials
Borealis Innovation Centre Linz 2009
We are taking steps …

• In 2007-2009 more than 80 scientists, engineers & technicians will be hired for IC Linz

• The equipment in the areas of analytics, characterization, testing and processing is being expanded (WAXS, $^{13}$C-NMR, AFM, multilayer extrusion, meltblown fibers, …)

• Cooperation with Austrian & International universities is being intensified
A glimpse into the future: Core-shell nanoparticles

Mineral core + chemically coupled polymer shell – possibly the next generation of impact modification with controlled nanostructure

(patent application filed)
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