Polymer Isolation as important process step in rubber production processes

Michael Bartke / Fraunhofer Polmyer Pilot Plant Center, Schkopau
List Symposia „Better than Steam“, Arisdorf, 22.10.2015
Fraunhofer Society in a nutshell..

The Fraunhofer-Gesellschaft promotes and conducts applied research in an international context, to benefit private and public enterprise and is an asset to society as a whole.

- Nearly 24,000 staff
- 66 institutes and research units

Research budget in 2014:
- 2 Mrd
- 1.7 Mrd

Close to 30% base funding by German federal and Länder governments

More than 70% contract research on behalf of industry and by publicly funded projects
What is the Fraunhofer Polymer Pilot Plant Center?

- A joint initiative of the Fraunhofer institutes for Applied Polymer Research (IAP) and Mechanics of Materials (IWM)
- Contract research in synthesis and processing of polymers in pilot scale
- Staff:
  - 18 FTE in polymer synthesis
  - 13 FTE in polymer processing
- Annual budget about 4 Mio €
Location: Schkopau

- 180 km south of Berlin
- 35 km west of Leipzig
- 15 km south of Halle

- long tradition in polymers...
Fraunhofer PAZ - 10\textsuperscript{th} year anniversary 19.10.2015
Fraunhofer PAZ - 10th year anniversary 19.10.2015
Fraunhofer PAZ - 10th year anniversary 19.10.2015
Polymerization Pilot Plant

- solution polymerization
- emulsion polymerization
- suspension polymerization
- polycondensation
- continuous polyester line
- hydrogenation

A flexible multiproduct-, multipurpose pilot plant
Polymerization Pilot Plant

- size main reactors: 50 – 1000 l
- infrastructure:
  - safety
  - waste gas combustion
  - waste water treatment
  - flexible process control system
- continuous operation possible
- fully registered chemical pilot plant
Working areas & customers

- **Polymer producer**
  - Contract synthesis
    - product development
    - application testing
  - Material Science
    - structure- / property relationships
    - polymer processing
    - testing & evaluation
  - Process development
    - new processes / process steps
    - scale up studies
    - kinetic & thermodynamic data
    - safety studies
    - modelling & simulation

- **Polymer converters**
- **suppliers** (e.g. catalysts, additives)
- **Engineering companies**
Synthetic rubber

- economically important polymers, approx. 14 Mio t/a production growth rate approx. 5%
- one main application: tires
- modern high performance rubbers with **controlled micro structure** are produced either via **anionic** or **coordinative solution polymerization**
- historically important working area in Schkopau
  - first industrial production of synthetic rubber “Buna” in 1937
- important working area at Fraunhofer Polymer Pilot Plant Center
Solution polymerization line
Solution polymerization line
Pilot experience synthetic rubber and related polymers

- BR coordinative continuously
- SBR anionic batch or continuously
- blockcopolymers anionic batch
- multiblockcopolymers anionic batch
- hydrogenation of multiblockcopolymers
- polymer isolation

Polymer isolation

- Why? → without polymer isolation, no product!
- polymer isolation is important for process economics
- Important: synthetic rubbers are temperature-sensitive products
Solution polymerization with polymer isolation

- Circulation solvent approx. 4..9 x production capacity of synthetic rubber
- Overall process efficiency depends strongly on the process efficiency of polymer isolation and solvent purification
Rubber isolation technologies at Fraunhofer Polymer Pilot Plant Center:

- industrial standard: coagulation / stripping
- direct devolatilization in kneader reactors
- new development by Fraunhofer: stripping with short residence time
Industrial standard: coagulation / stripping

Purification / drying

Purification / drying

polymerization

coagulation / stripping

rubber drying

Total energy consumption:
Approx. 40% for solvent removal, approx. 40% for solvent purification
Industrial standard: coagulation / stripping

- complex, a lot of equipment, high space requirement…
Coagulation / Stripping in pilot scale

- Coagulation / stripping is available in the Pilot Plant Center since opening in 2005

- Scale-down and operation is problematic:
  e.g. rubber crumb size vs. piping size and fluid velocity:

  ![Diagram showing agglomeration / plugging processes](image)

- Improvement of operability via continuous fine tuning:
  - Realization of a circulation loop in order to enable high velocities with adequate pipe diameters
  - Fluid dynamics in coagulator
Coagulation / Stripping in pilot scale

- some improvement of operability
- but still complex and not easy to operate…
Direct devolatilization

- Waterfree isolation of the polymer via direct devolatilization of the solvent in kneader reactors – process developed and owned by List AG:

Advantages:
- no water phase
- no solvent drying needed $\Rightarrow$ significant energy savings
List Kneader Reactors @ PAZ

C2610 - CME
CME 100 CONTI – hydraulic driven
- 100 Liter volume
- 2,1 m² heat transfer area
- L : D – 1,8 : 1
- ADS 54 for discharge

C3610 - CRP
CRP 160 CONTI – hydraulic driven
- 200 Liter volume
- 7,2 m² heat transfer area
- L : D – 6,3/3,9 : 1
- ADS 54 for discharge

Used @ PAZ for e.g.:
- devolatization
- polycondensations
- bulk polymerizations
Kneader Reactors
Direct devolatilization

- In a number of pilot campaigns for LIST AG at Fraunhofer, the process has been demonstrated and developed further:
  Starting point: two stage direct devolatilization

- Main evaporation in the 1\textsuperscript{st} kneader
- Degassing in the 2\textsuperscript{nd} kneader
Direct devolatilization

Modification I:

Feedsplitting main evaporator + water dosing to degassing:

Advantages: better temperature control, steam as "carrier gas" ⇒ lower solvent residuals, higher throughput, no vacuum required

Disadvantages: contamination of solvent with water – but only of a small fraction of solvent...
Direct devolatilization

Modification II: Pre-concentration flash prior to direct devolatilization

Advantages: Substitution of electrical energy with steam
Increase of throughput / maximum line capacity
Direct devolatilization

Modification III: Confectioning

Advantages: Product as bales – important for customer acceptance …
Impressions

- 60 tons of polymer solution processed in two weeks...
Impressions

- Process window tested

26-Vak-02-200-HL09
Direct devolatilization

Advantages:

- No product damaging, excellent product qualities confirmed by several rubber producers
- Significant energy savings
- Significant simplified plant design
  \[ \rightarrow \text{process ready for commercial realization} \]

Disadvantages:

- No washing-effect compared to coagulation & stripping
New process: stripping with short residence time

- Experimentally developed at Fraunhofer starting from the operational difficulties with traditional coagulation / stripping
- Main idea: Generation of very small primary particles, which degases fast
Realization: Stripping with short residence time
New process: stripping with short residence time

- Successfully applied in a number of campaigns
- Reduction of solvent residues down to spec (<500 ppm) demonstrated
- Patent application filed

Advantages:
- Can be adopted to new products fast, robust operation
- Very short residence time, approx. 40 s compared to 0.5 h - 2 h for other technologies
  - Significant smaller equipment
  - Lower investment costs and space requirements
  - Lower hold-up, fast product changes, easy to clean
New process: stripping with short residence time

Disadvantages:
- Similar to traditional coagulation/stripping, solvent is contaminated with water

Status:
- First license for pilot operations sold
- For commercial operation, energy optimization required
New process: stripping with short residence time

- Approx. 10% of water residues in polymer ⇒ drying required
- One possibility: for small batches belt-dryer
- For larger batches: LIST Kneader as dryer

Advantages List Kneader as dryer:

- Higher throughput
- Reduced space requirements
- Closed system – no dryer off gas which needs to be incinerated
- Vacuum possible

⇒ drying at lower temperatures – prevent product damages for temperature sensitive products
Summary
Polymer isolation is an important process step for solution polymerization
Different polymer isolation processes for rubber solutions at Fraunhofer PAZ

coagulation / stripping
- industrial standard
- scale-down is difficult, some improvement of operability by fine tuning

direct devolatilization in kneader reactors:
- very energy efficient process of List AG
- excellent product qualities confirmed
- good operability, ready for market introduction

stripping with short residence time
- New development by Fraunhofer, patent application filed
- very short residence time compared to other processes
- well suited for pilot operation
Thank you for your attention!
www.polymer-pilotplants.com