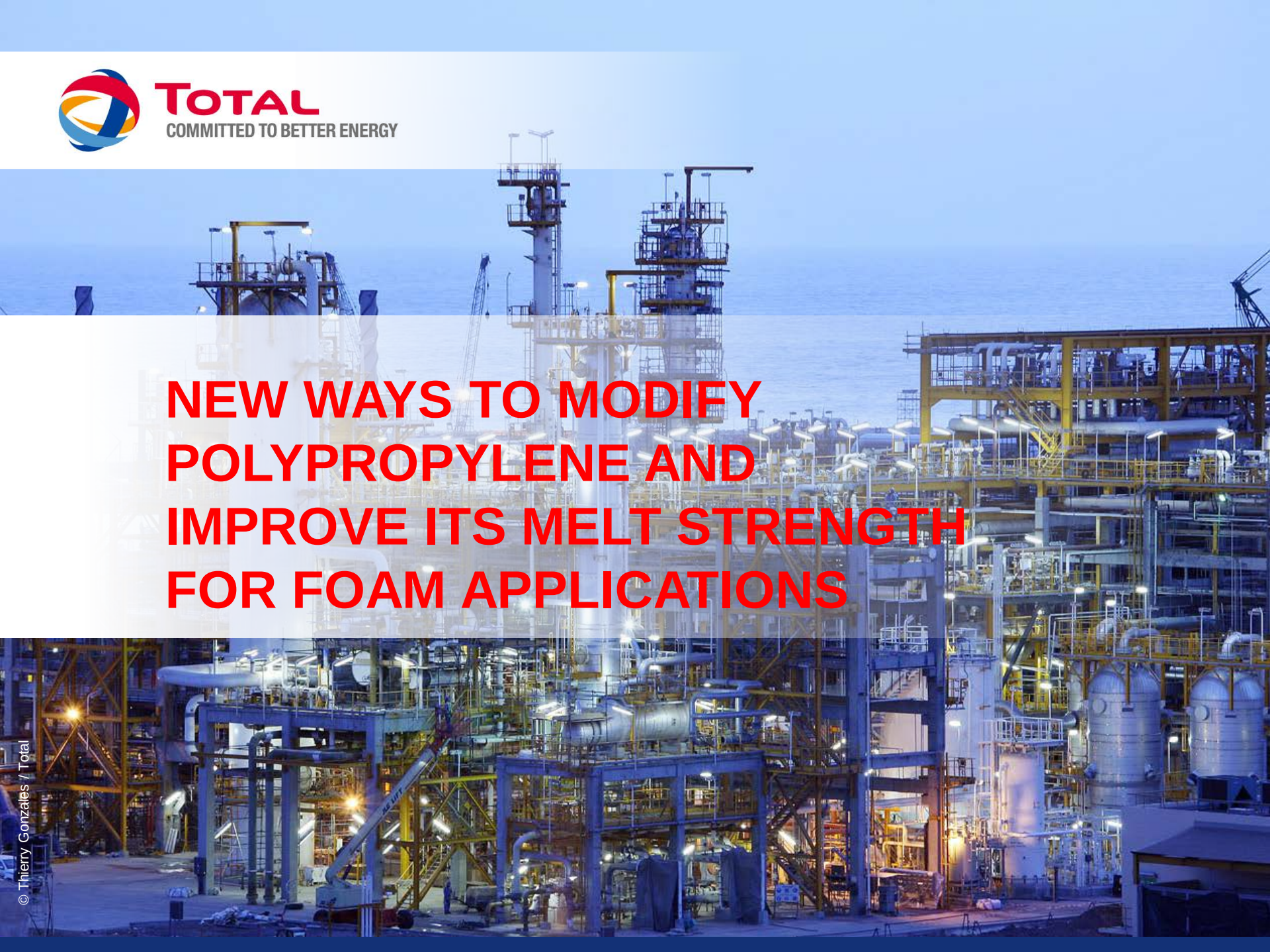
TOTAL
COMMITTED TO BETTER ENERGY

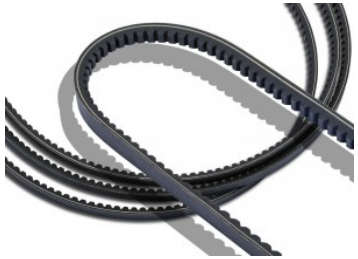
NEW WAYS TO MODIFY POLYPROPYLENE AND IMPROVE ITS MELT STRENGTH FOR FOAM APPLICATIONS

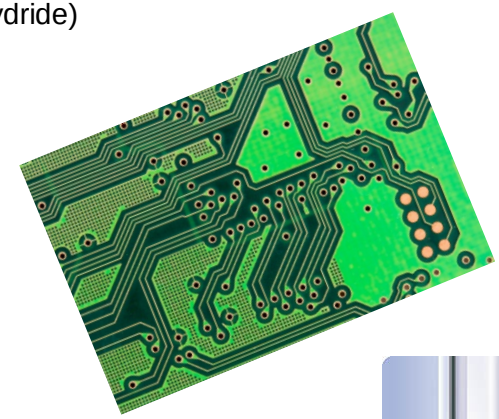


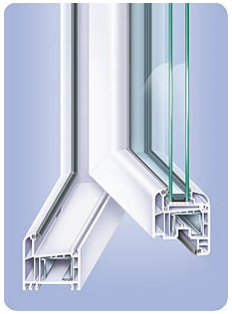
TOTAL CRAY VALLEY

CRAY VALLEY
A BRAND OF TOTAL

- Speciality resin supplier
  - C4 resins
  - C5 resins
  - C9- pure monomers
  - SMA (Styrene Maleic Anhydride)
  - Zinc salts

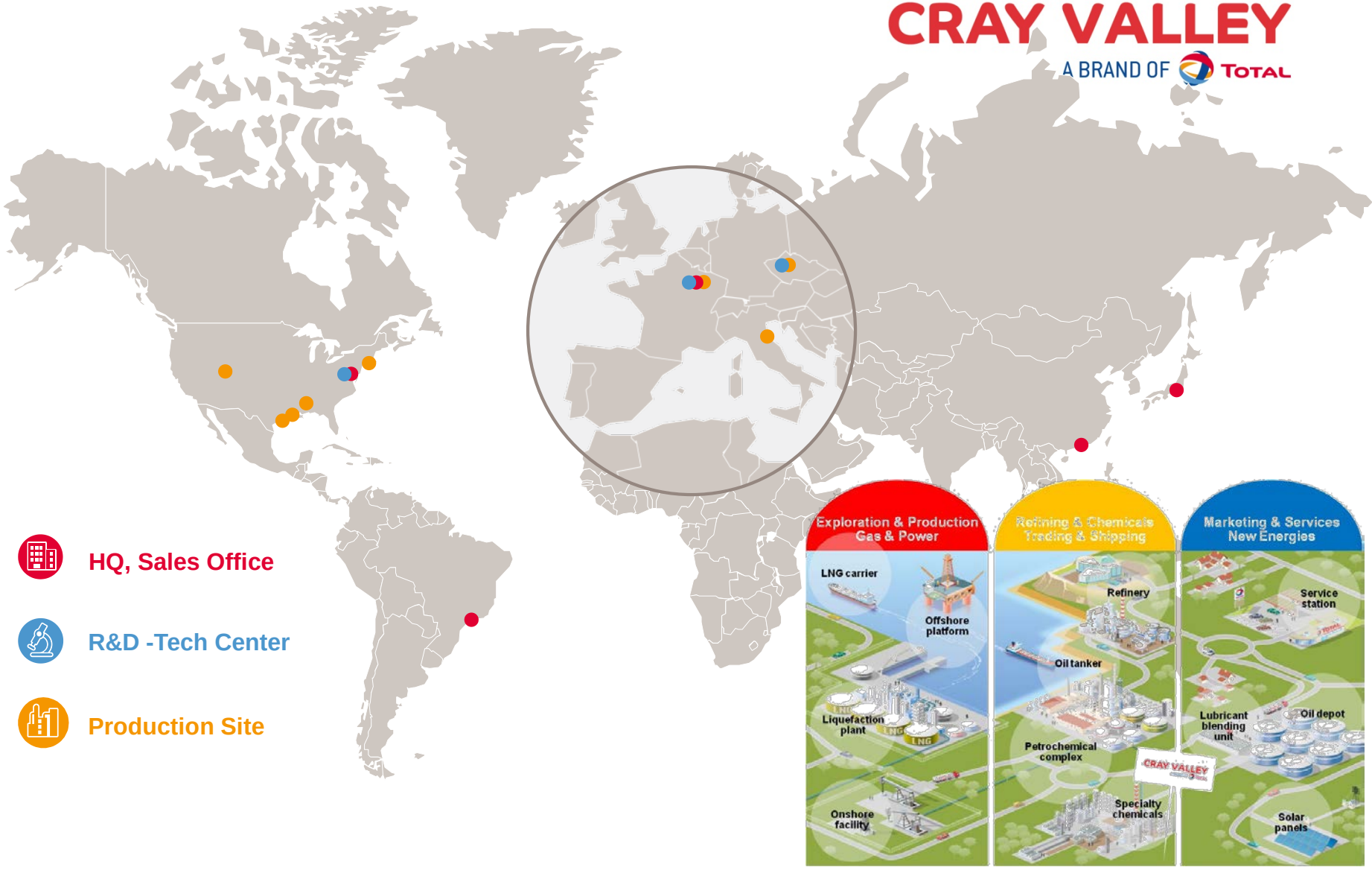






TOTAL CRAY VALLEY

CRAY VALLEY
A BRAND OF TOTAL



HQ, Sales Office

R&D -Tech Center

Production Site

PP FOAMING

USUAL PP PROPERTIES

- Wide range of industrial products
  - Homopolymer, Random Copolymers (C4, C6,…) or Impact copolymers
  - Dedicated additivations
    - Nucleation, Anti-static, heat stability
- Wide potential for control by:
  - Catalyst type and selection (Ziegler-Natta or metallocene)
  - Process fine-tuning

	Homopolymers	R-Copolymers	I-Copolymers
Viscosity	0.3 – 150 g/10min	1-100 g/10min	0.3-100 g/10min
Modulus	1300-1800 MPa	850-1250 MPa	900-1600 MPa
Melting point	<165°C (controlled by nucleating agents)	130-159°C	<160°C

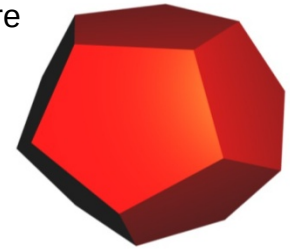
Melt-Strength is still difficult to obtain…

MELT STRENGTH

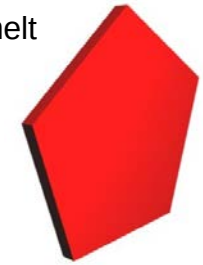
- Degree of resistance to extensional flow
- Ability of a molten polymer to keep its integrity under flow
- Melt strength means the force needed in extension to break the polymer melt*

Resistance while flowing & « elongation at break »
during foaming process

Internal or external pressure



Thin film melt elongation resistance



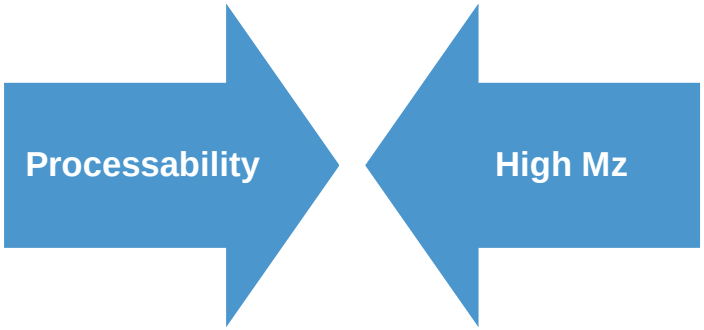
Hundreds of microns to microns thickness

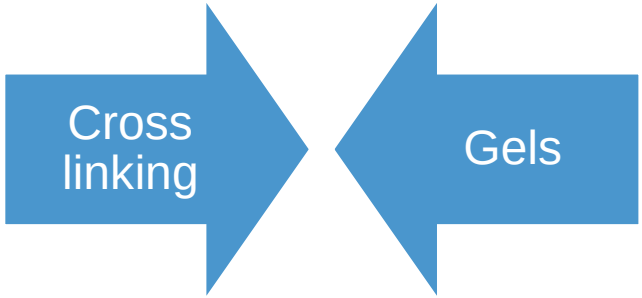
The influence of molecular weight distribution of industrial polystyrene on its melt extensional and ultimate properties. M. Shivokhin, C. Bailly

* US6875826 B1

HOW TO IMPROVE PP MELT STRENGTH?

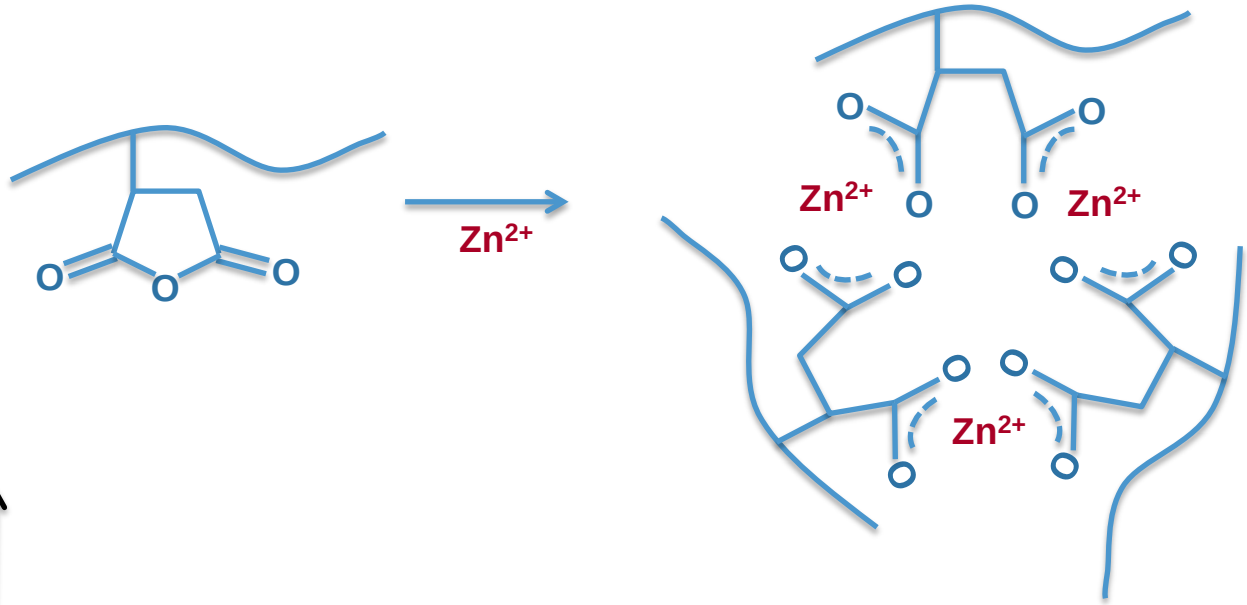
In-Reactor modification	Post modification
• Increase high molecular weight fractions	• Introduce long chain branching, crosslink, modify chain-chain interactions
Catalyst and process tuning	Chemical or E-beam X-linking (peroxides, coagents). Macromonomer grafting Chemical modification.

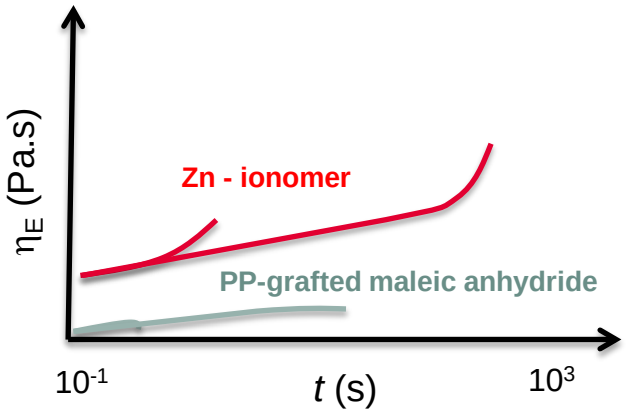




…a difficult balance

NON CLASSICAL ROUTES





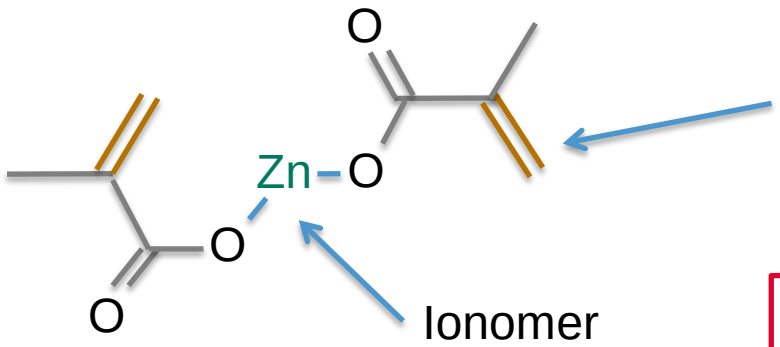
Very significant effect on:
- Expansion ratio
- Morphology

Li et al., Polymer 70 (2015), 207

DYMALINK® ADDITIVES FOR IONIC X-LINKING OF POLYPROPYLENE

DYMALINK® 9200

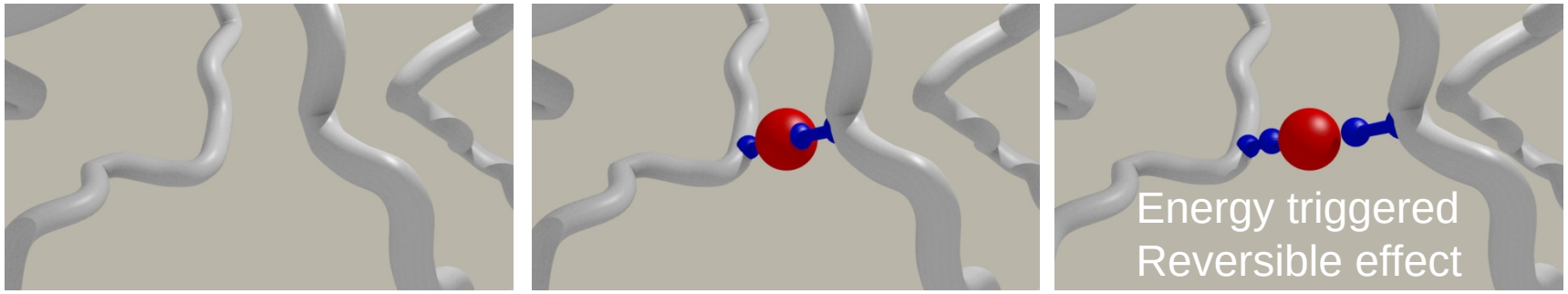
- Zinc diacrylate salt (available in MB as 9201)



Reactive functions

Ionomer

Extrusion temperature > 220°C
Grafting even without peroxides



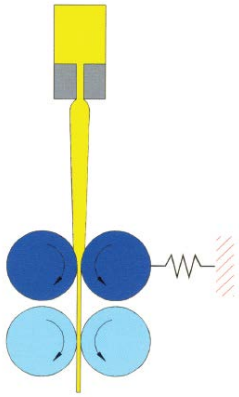
STUDY BASICS

neat PP (MI 3,5 g/10min)
2500 ppm AOX package
500 ppm Ca Stearate

+

0,5% - 2%
Dymalink® 9200

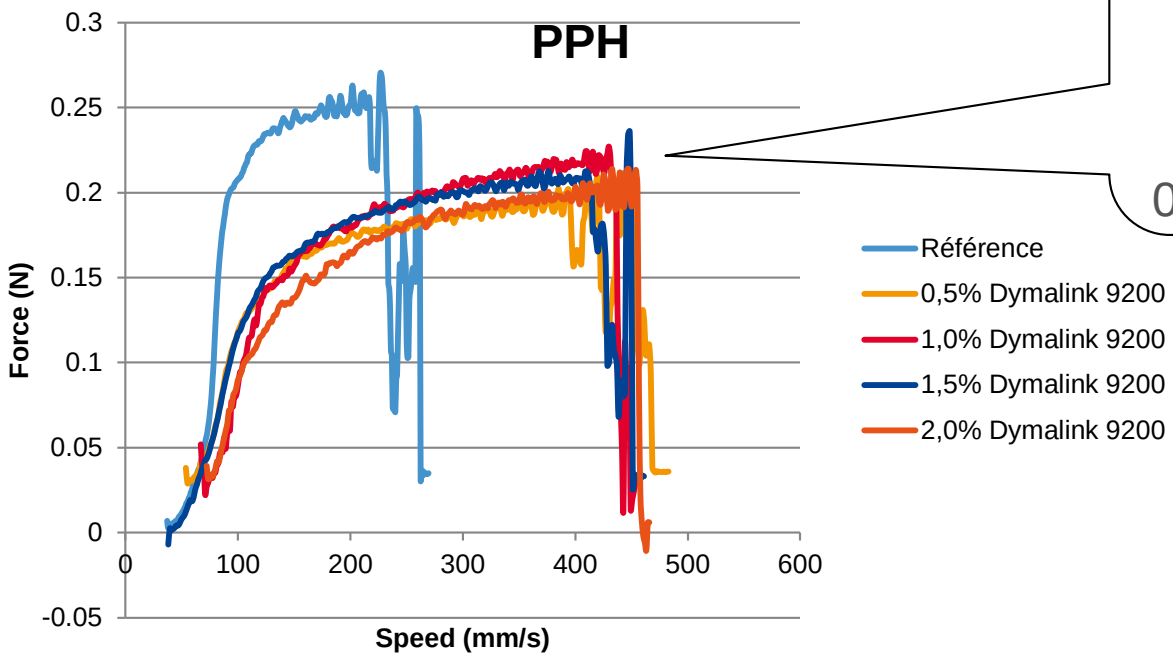
Molecular characterization
Properties



GPC (MWD)
DSC (Crystallization)
Rheology
Mechanical Testing

RESULTS – MELT STRENGTH

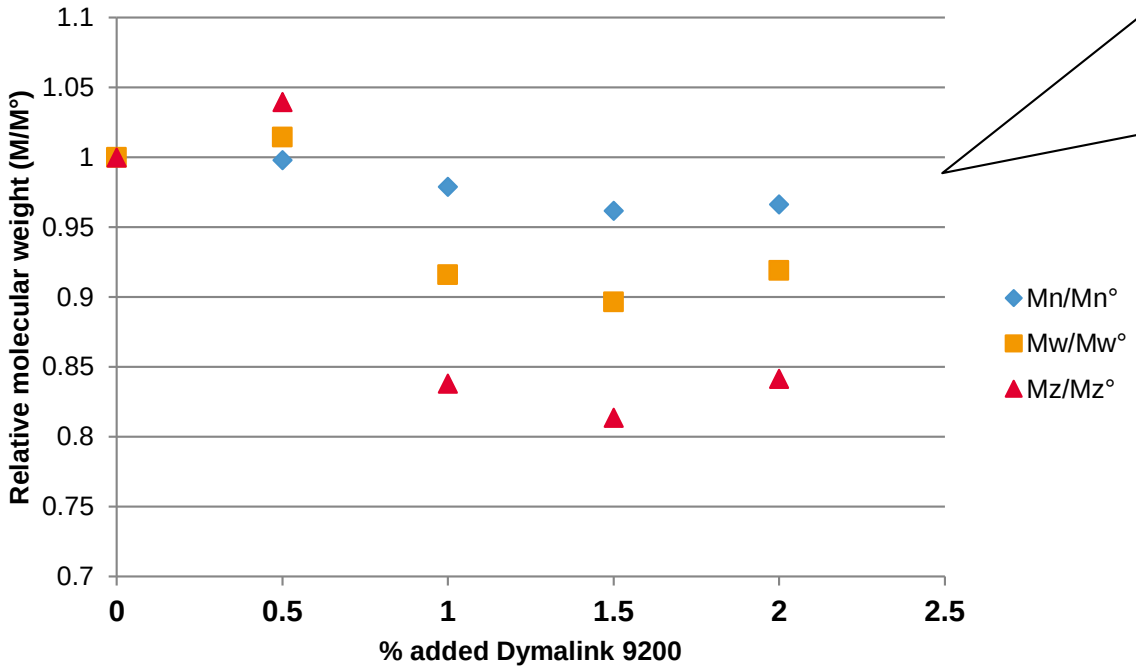
- Rheotens 71.97 Göttfert
- 2mm die, L/D 15, controlled temperature and pressure



Melt elongation improved. Effect observed at 0.5% DL9200

MOLECULAR WEIGHT

- PP is known to undergo chain scission
- Maleinated or peroxides treated PP can exhibit increased low molecular weight fraction



- Slight increase at 0.5% Dymalink®
- Moderate decrease for Dymalink® % > 2%
- Mn values not dropping

We are analyzing ionomers in a polar solvant…

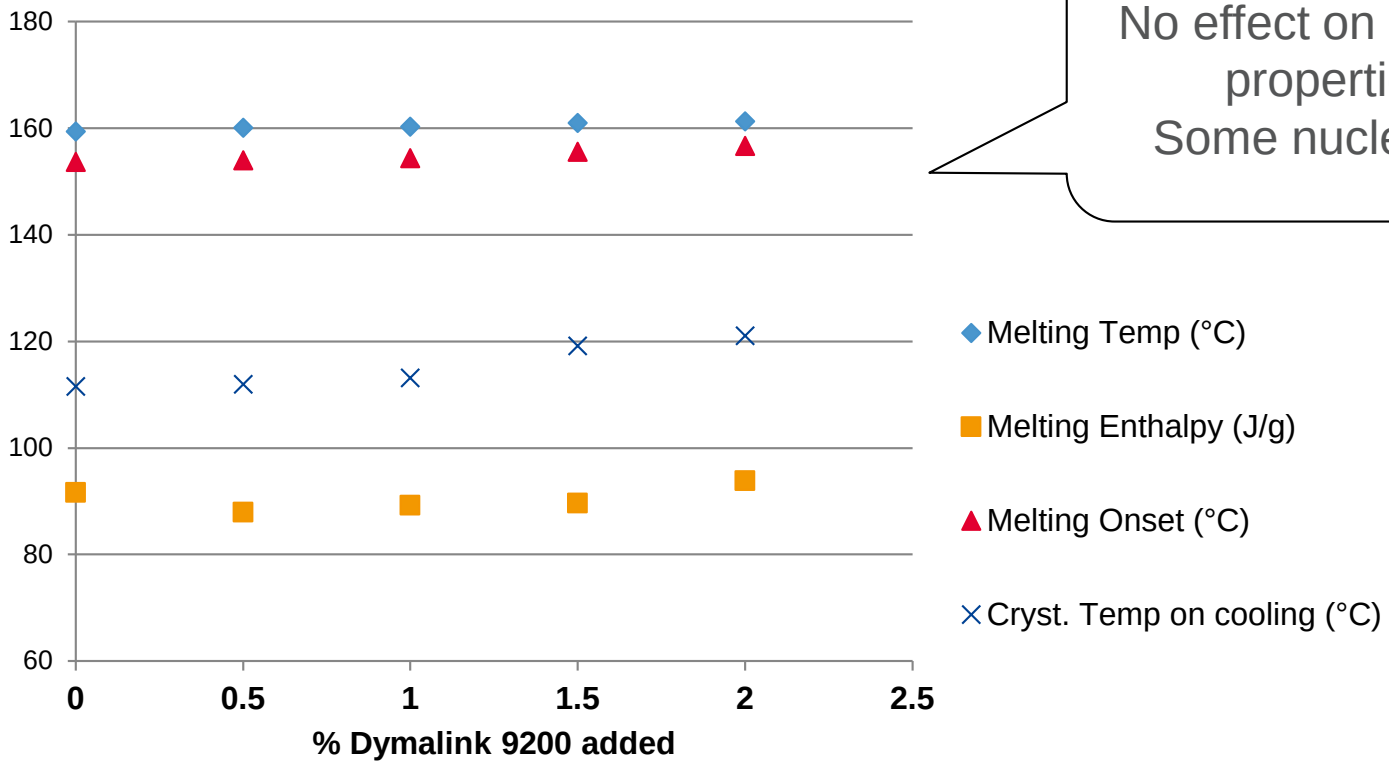
RESULTS – DYNAMIC RHEOLOGY

- g rheo approach[1]
- Correlations between MWD-cross over points and Carreau-Yasuda parameters for linear and LCB PP

PPH	0%	0.5%	1.0%	2.0%
η_0	11,8 k	11, 3 k	13,4 k	16,7 k
Mn	62,1 k	62,1 k	62,1 k	61,2 k
Mz	2.090 k	1.848 k	1.762 k	1.565 k
g rheo	0.96	0.93	0.91	0.88

1 Jacques Michel, Antec 2002, http://www.4spe.org/Resources/resource.aspx?ItemNumber=10936

CRYSTALLINITY

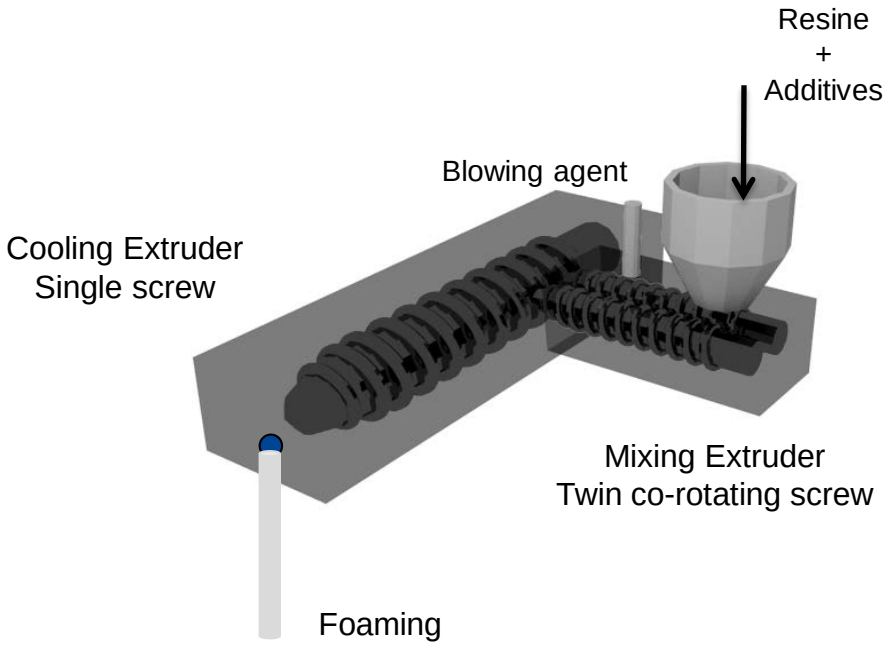


No effect on melting properties
Some nucleation

- Zinc salts have been reported in the literature as efficient nucleating agents
- We do not observe any crystallization slowing down due to ionomers

FOAM APPLICATIONS

- Tandem foaming line
- Formulation :
  - Resin PPH 3,5MI
  - Talc (0.5%)
  - Blowing agent (up to 4%)
  - HMS additives (up to 5%)
- Parameters evaluated:
  - Double-screw and SS extruder temperature
  - Screw speed rates
  - Blowing agent type and quantity (CO_2, Butane)
  - HMS additive type and quantity (Market reference, Dymalink® 9200)

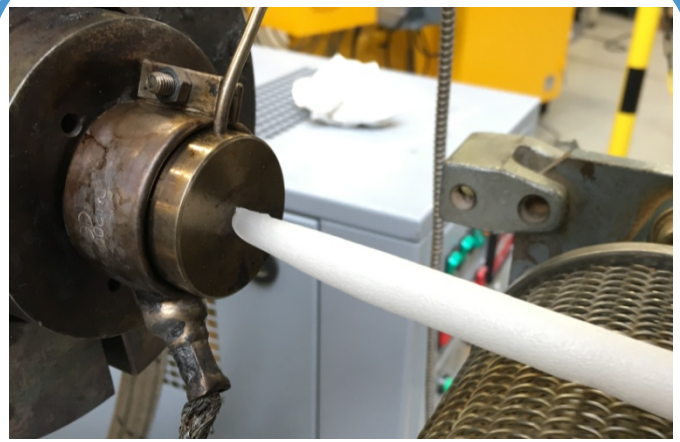


Foaming behaviour

Neat < reference ~ PP + Dymalink ® 9200

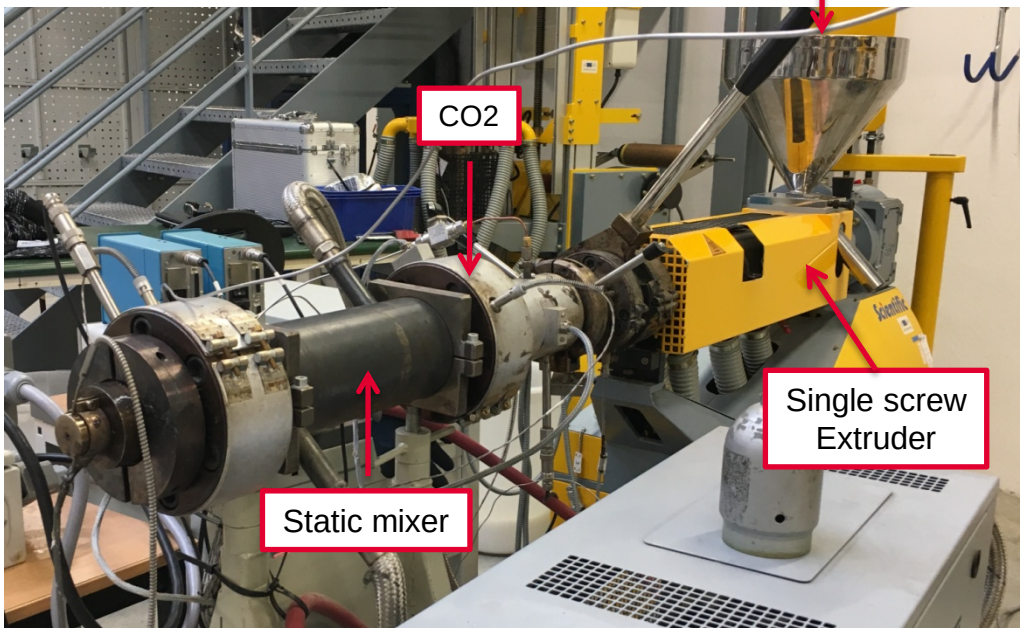
FOAM APPLICATIONS

- Single screw extruder + static mixer
  - PP already compounded at 240°C
  - CO_2 injected in liquid form – P>74bar
  - Better control of the cooling temperature

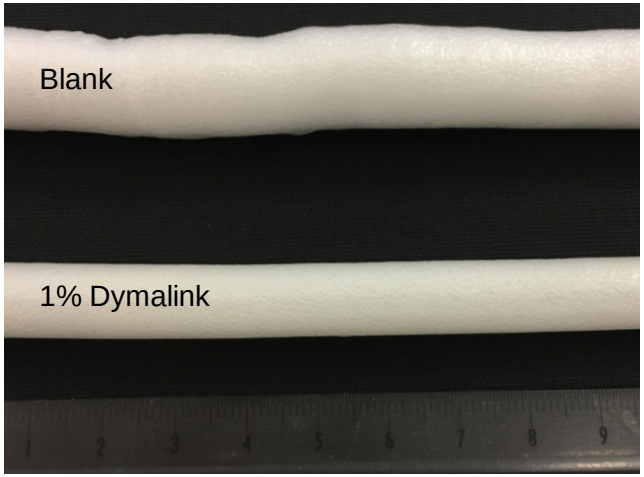


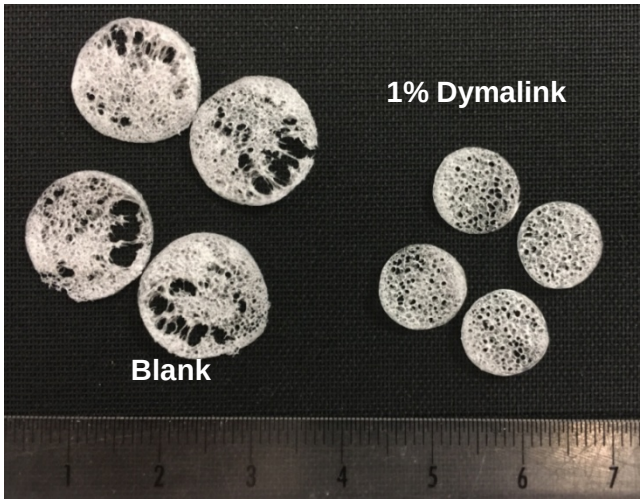
Foaming step :

1) PP is extruded
2) Expansion
3) Skin formation



FOAM APPLICATIONS





In presence of Dymalink ® 9200:

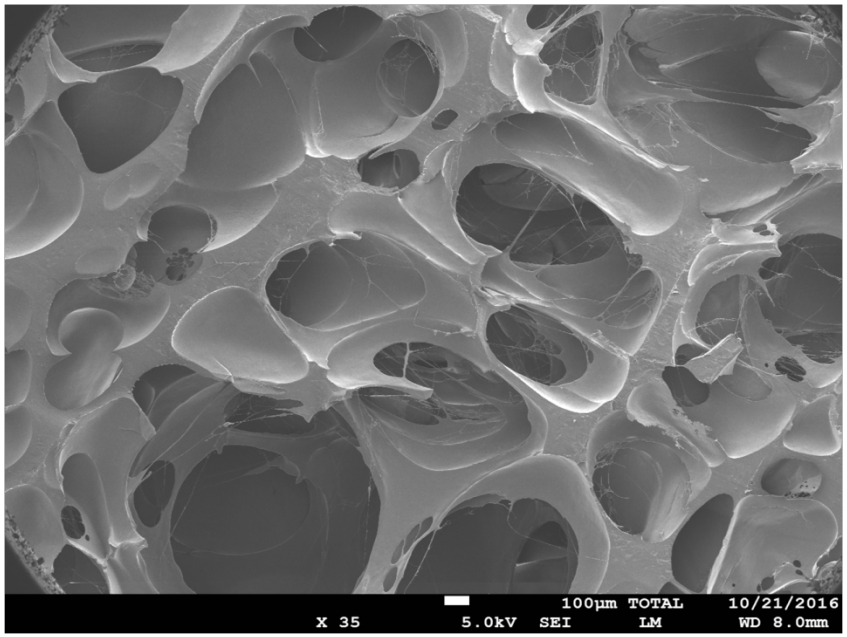
Extruded foam rods:
1) Stable extrusion
2) Nice skin

Cells:
1) Higher density
2) More homogeneous

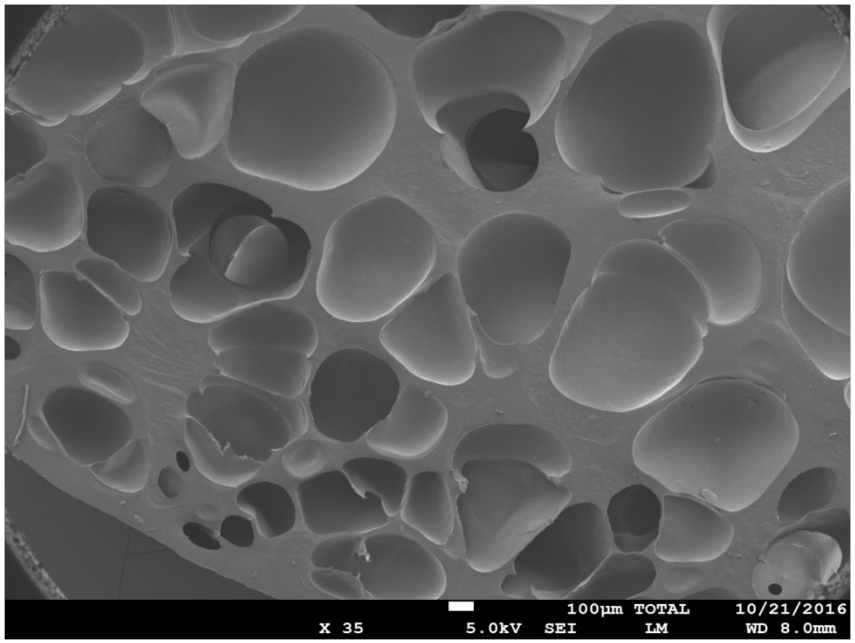
- **Benefits**
  - Modification of the morphology
  - Enhance working window

FOAM APPLICATIONS

- Morphology



PP+Talc - p. die 130 bar,
$C0_2$ 0.6mL/min



PP+Talc+ 1% Dymalink 9200 –
p. die 125 bar,
$C0_2$ 0.6mL/min

CONCLUSIONS

- An improved melt strength PP can be obtained with Dymalink© 9200
- Very few observed drawbacks vs neat PP
- Freedom to tailor the compound
- Dymalink 9200 is commercialy available in
  - US , EU and Asia

US20150031838 *: Metallic acrylate salts to increase polymer melt strength

Thanks to Contributors:
Total Research and Technology Feluy
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