# Tyre devulcanized rubber (dGTR) : evolution of its characteristics over time

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Pôle de compétitivité caoutchouc

HORIZON 2020

# Outline

- Phénix-Technologies : a general presentation
- Recycling methods
  - Micronisation
  - Devulcanisation
- Characteristics of dGTR
- Uses of dGTR
- Evolution of dGTR characteristics over time
- Experienced issues
- New developments
- Conclusion

# Phénix-Technologies : general presentation

- Phénix is located in Sancheville, France


- Member of various associations:
  - Elastopôle (French cluster on Elastomers)
  - AFICEP ( Rubber Engineers Association)
  - ASTM (American Society for Testing Materials)
  - Sustainable materials group (ARTIS)

- Active in elastomer recycling area
  - Rubber granulation / pulverisation / micronisation
  - Devulcanisation by reactive extrusion assisted or not by $scCO_2$

- Consulting: secondary raw materials produced by ELT's Thermolysis

- Founder and single participant of the European project "DEVULC" (H2020, from April 2015 to May 2018)

DEVULC

HORIZON 2020
LE PROGRAMME DE RECHERCHE ET D'INNOVATION DE L'UNION EUROPÉENNE

# Phénix-Technologies : general presentation

## Granulation-Pulverisation-Micronisation
## Densimetric and electrostatic separation

Granulator - Pulveriser - Micronisers

## Devulcanisation unit


## 3 Twin screw extruders

- For devulcanisation testing (27 mm) : coupled with a $CO_2$ pump
- For TPE-V testing (40 mm)
- For devulc processing at an industrial scale 65 mm

# Phénix-Technologies : general presentation

## Laboratory Material Characterisation:

- Viscometer Mooney MV 2000 - Alpha tech.
- Rheometer MDR Pioneer - Alpha tech.
- TGA2 - Mettler Toledo
- FTIR Is10 - Thermo Scientific
- Coupling line TGA-IR
- Mechanical testing (traction, compression, tear strength …) - AGS-X Shimadzu
- Hardness tester Shore A

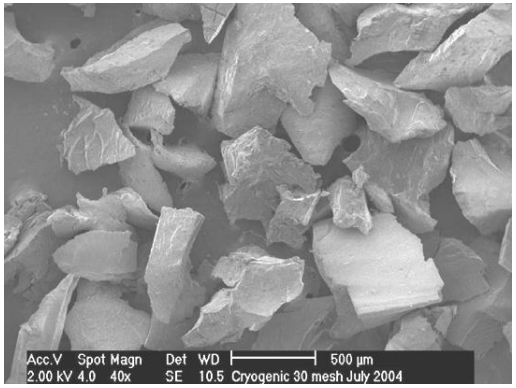
## Rubber shaping:

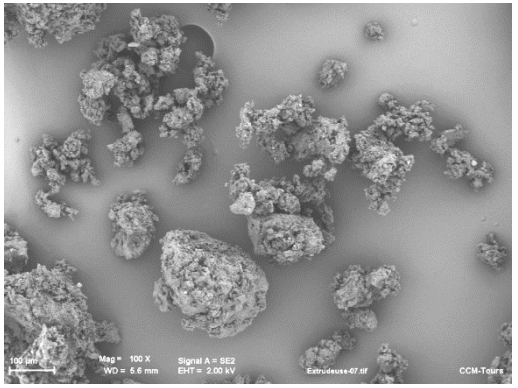
- Lab mixing mill (cylinders)
- Vulcanisation press
- Moulds

# Recycling methods

## Micronisation

| SEPARATION BY PARTICLE SIZE | | |
|---|---|---|
| Fine Rubber Powders | < 800 µm | > 20 mesh |
| Micronised Rubber Designation : Mc | < 425 µm | > 40 mesh |



Cryogenic and ambient [1] ground rubber particles

[1]. Pehlken Alexandra, Essadiqi Elhachmi, Scrap Tire Recycling in Canada, CANMET Materials Technology Laboratory, 2005

# Recycling methods

## Micronisation

Micronised powder
~ 300µm (50 mesh)

Direct compression moulded

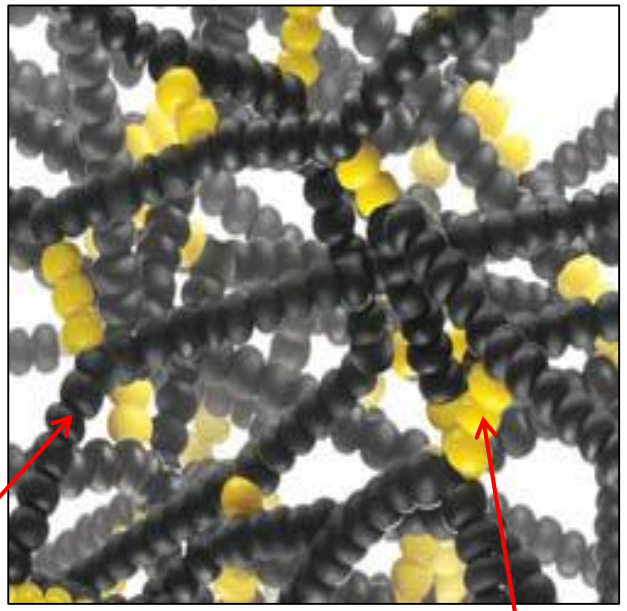
Incorporated in a rubber masterbatch and vulcanised
(example with EPDM)

# Recycling methods

## Devulcanisation

Existing Methods:

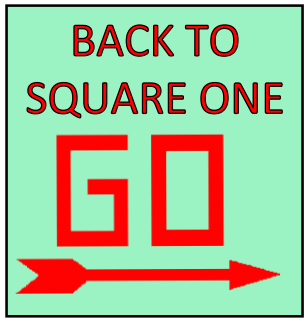
- Mechanical (with or without chemicals)
- Thermal (with or without chemicals)
- Physical (Ultrasounds, micro-waves)
- Chemical
- Micro-biological




Some of these techniques are either (or both):

- Leading to high material degradation (i.e excessive breaking of C-C bonds)
- Not economically or industrially viable
- Using harmful (and forbidden or about to be) chemical devulcanisation agents

# Recycling methods




Production scraps ***or*** end-of-life products

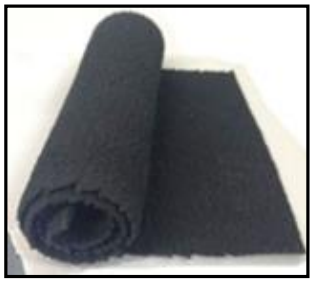
Granulation

New rubber products

**The rubber cycle**

+ Crosslinking agent
+ cure

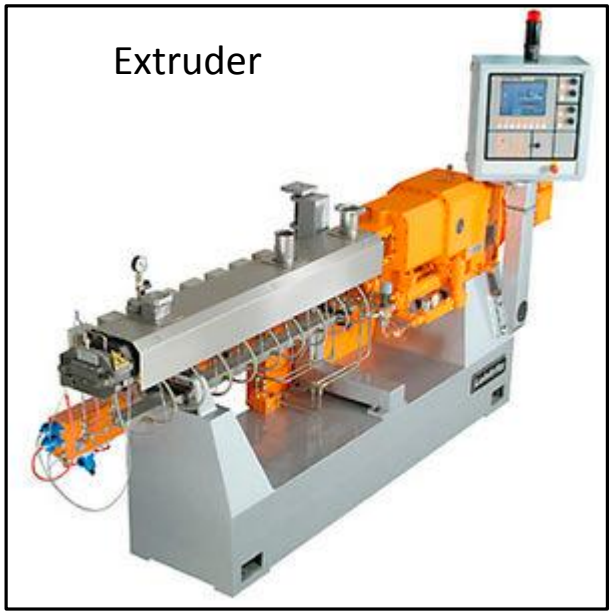
Devulcanised rubber



+ thermoplastic
(+ crosslinking agent)

Devulcanisation

Extruder



# Characteristics of dGTR

## Viscosity (ML (1+4)@100°

- The viscosity can be adjusted from 30 to 100 MU.
- The mechanical characteristics are degraded with the decrease of the viscosity

## Solubility in toluene

dGTR does not dissolve fully in toluene

➔ Rubber is not or partially degraded

## Mechanical caracteristics

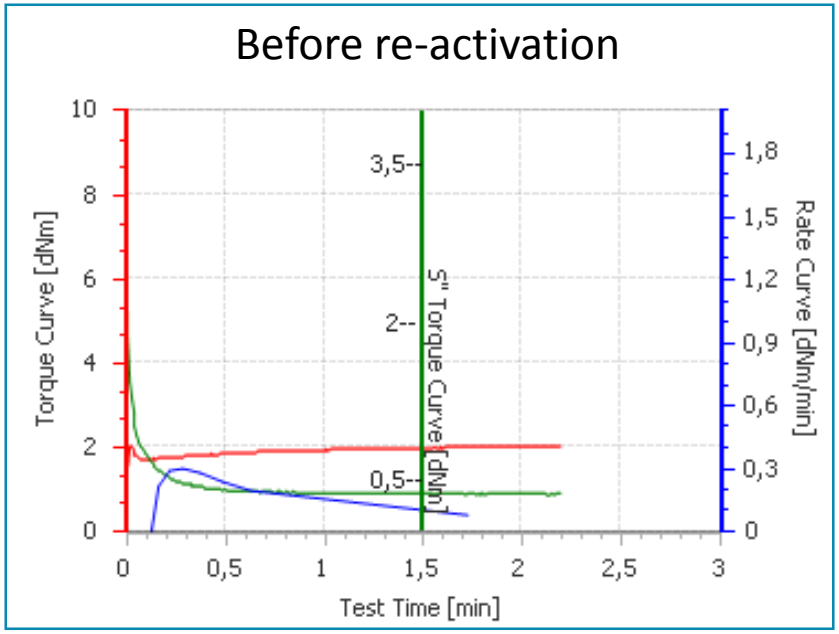
| | Tyre Tread (TT) | Whole tyre (TT) | Whole tyre (PC) |
|---|---|---|---|
| **Tensile strength (MPa)** | up to **18** | up to **12** | up to **8** |
| **Strain at break (%)** | up to **400** | up to **300** | up to **220** |

**These characteristics are obtained whether with or without CO2sc**

# Characteristics of dGTR

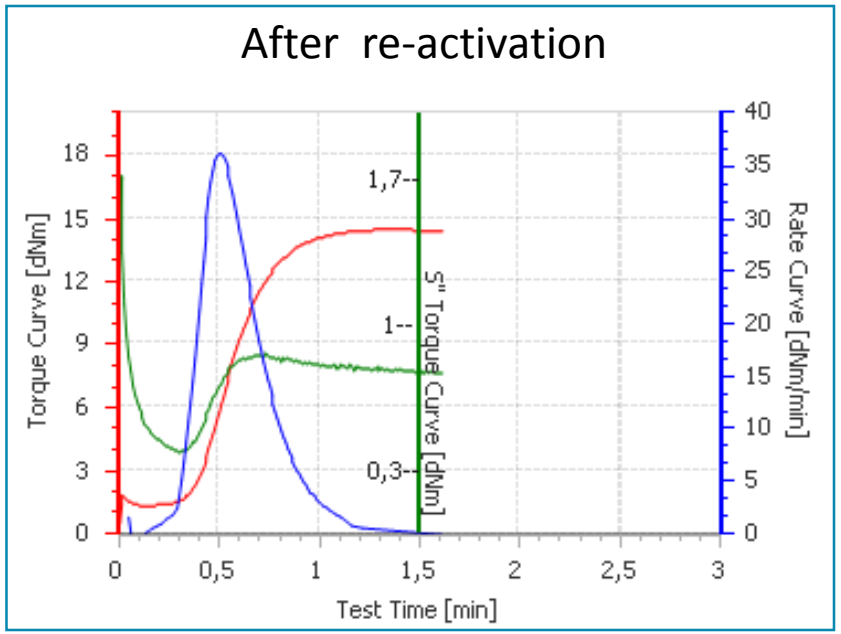
## MDR rheogram at 180°C

Before re-activation




+ Addition of curing agents

After re-activation



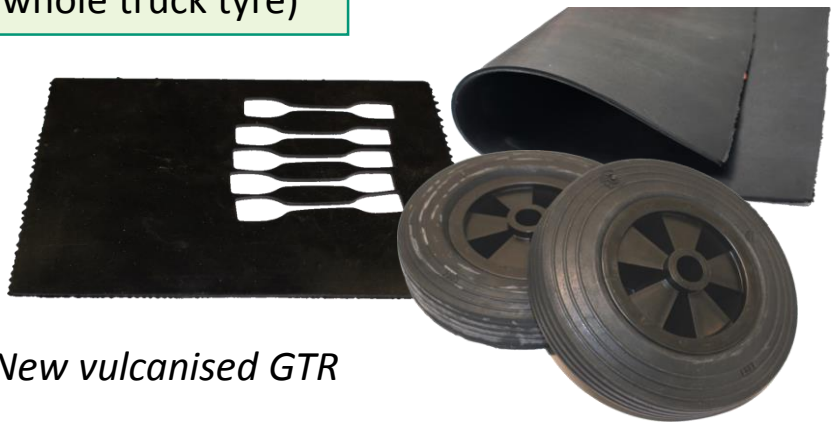

Red: Torque  Green : Viscosity, visco- elastic behaviour  Blue : Torque derivative

The devulcanised material behaves as a non-activated raw mix (flat MDR curve after devulcanisation) and, after re-activation, it behaves like an accelerated rubber mixture.

# Uses of dGTR

**1) Use of 100% devulcanised rubber**
Example: Ground Tyres Rubber (whole truck tyre)

*Devulcanised GTR*



*New vulcanised GTR*

| | Tensile strength (MPa) | Strain at break (%) |
|---|---|---|
| GTR 1 | 10.5 | 315 |
| GTR 2 | 11.6 | 246 |

- ✓ Low-cost materials
- ✓ Adjustable mechanical properties according to the formulation
- ✓ Can replace the virgin rubber in various applications (building, civil engineering…)

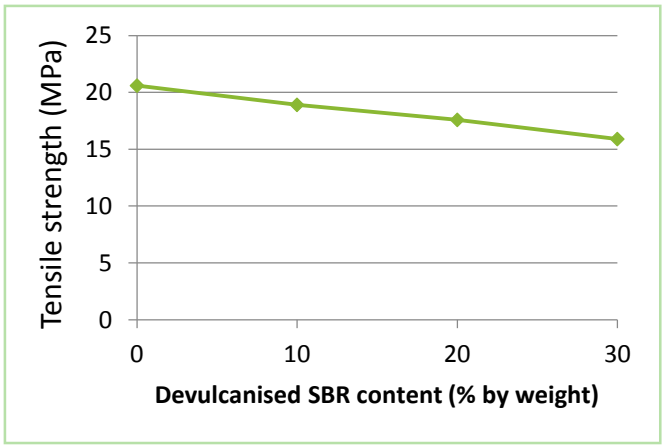
# Uses of dGTR

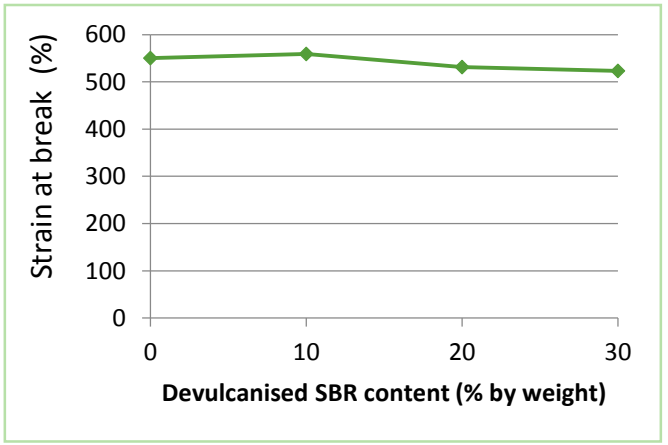
**2) Incorporated in a virgin rubber matrix**
Example 3: Styrene Butadiene Rubber (SBR)

*Devulcanised SBR*

*Raw SBR*

*New vulcanised SBR*




| | **Loss of properties at 30%** |
|---|---|
| Tensile strength (Mpa) | 22,8 % |
| Strain at break (%) | 5 % |

- ✓ ***Low degradation*** of the mechanical properties
- ✓ Allows to ***reduce the costs***

# Uses of dGTR

**3) Incorporated in a thermoplastic matrix**
Example: Thermoplastic vulcanisates (TPE)

*Devulcanised rubber*

*Thermoplastic*

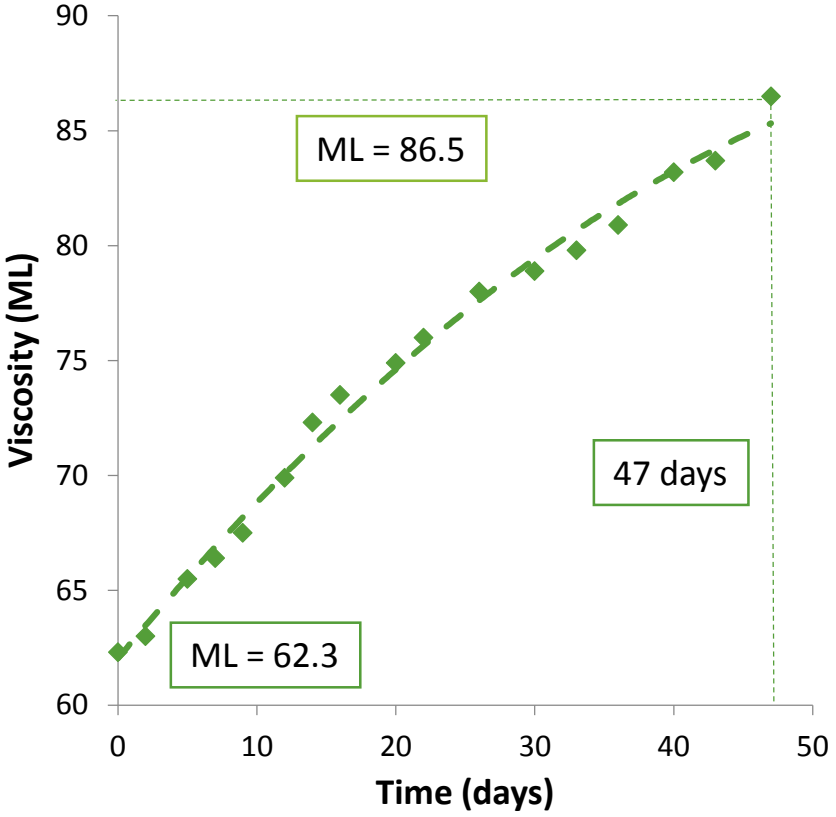
*Thermoplastic vulcanisates*

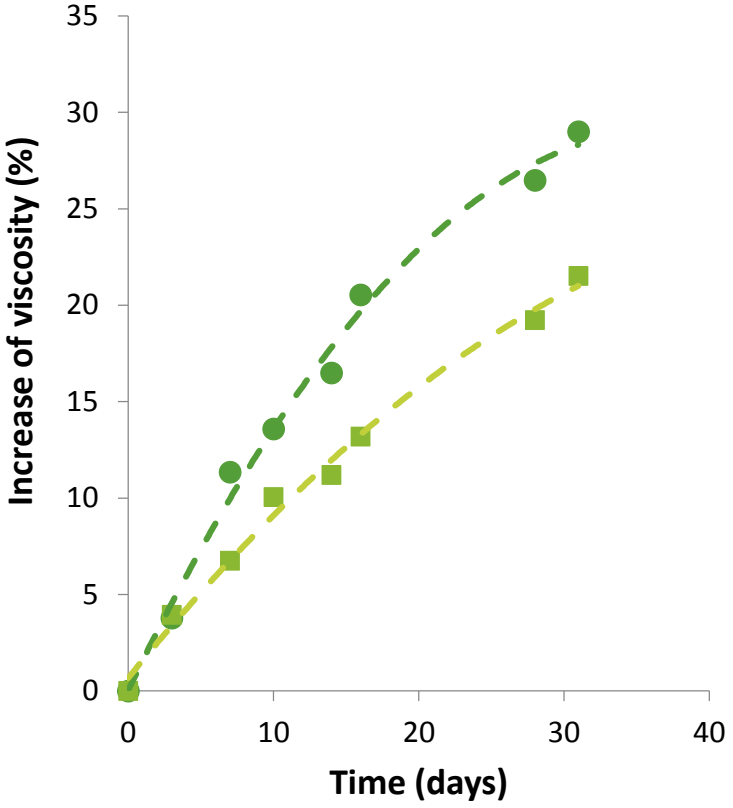
- ✓ Simplified processing
- ✓ Can be processed by extrusion, injection molding, blow molding or thermoforming
- ✓ Ease of scraps and waste recycling
- ✓ Can be easily colored when there is no carbon black content

# Evolution of dGTR characteristics over time

# Evolution of dGTR characteristics over time

(ambient temperature)



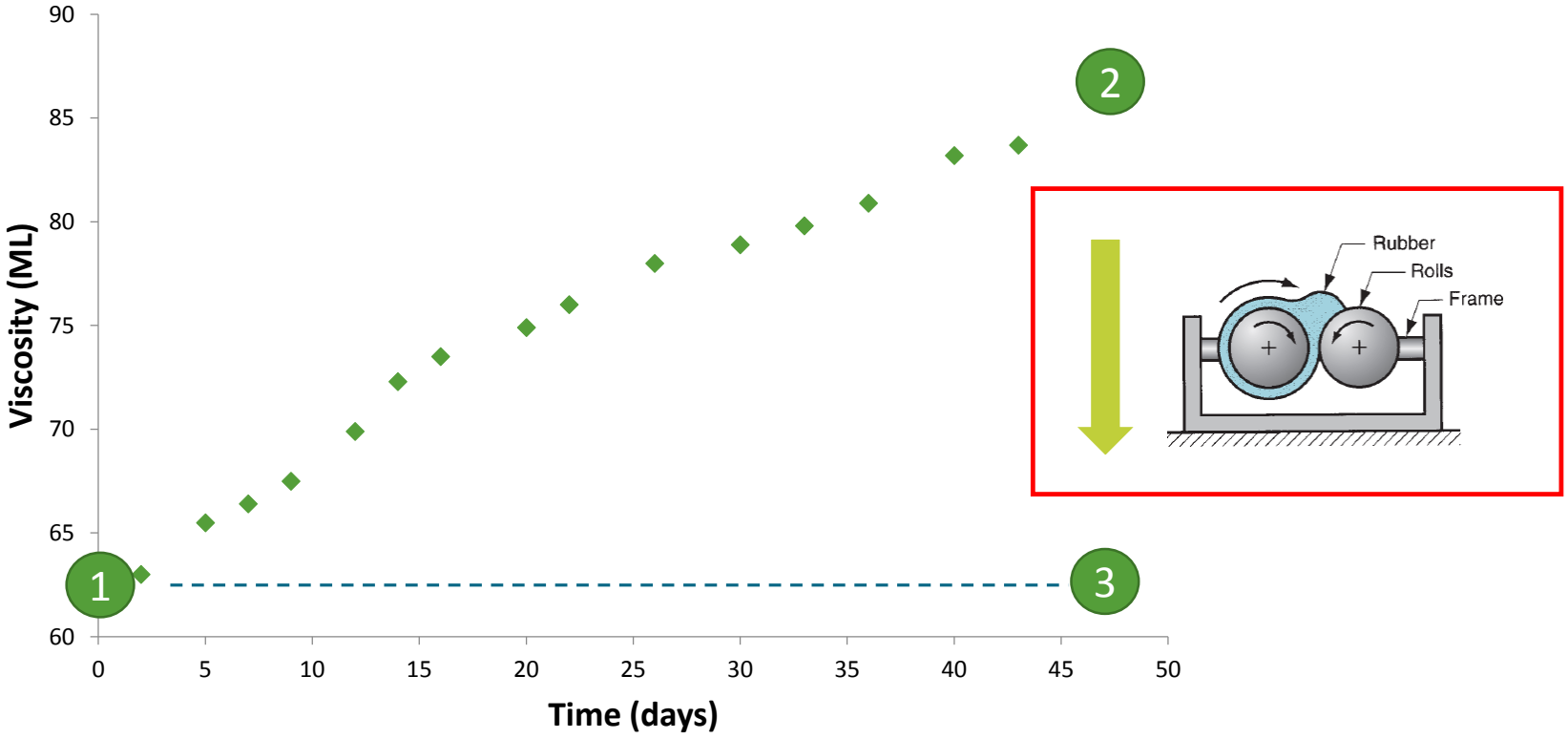




The increase rate of the viscosity depends on the type and the part of the vulcanized tyre

The increase of viscosity is observed regardless of the devulcanization method (with or without CO2sc)

# Evolution of dGTR characteristics over time

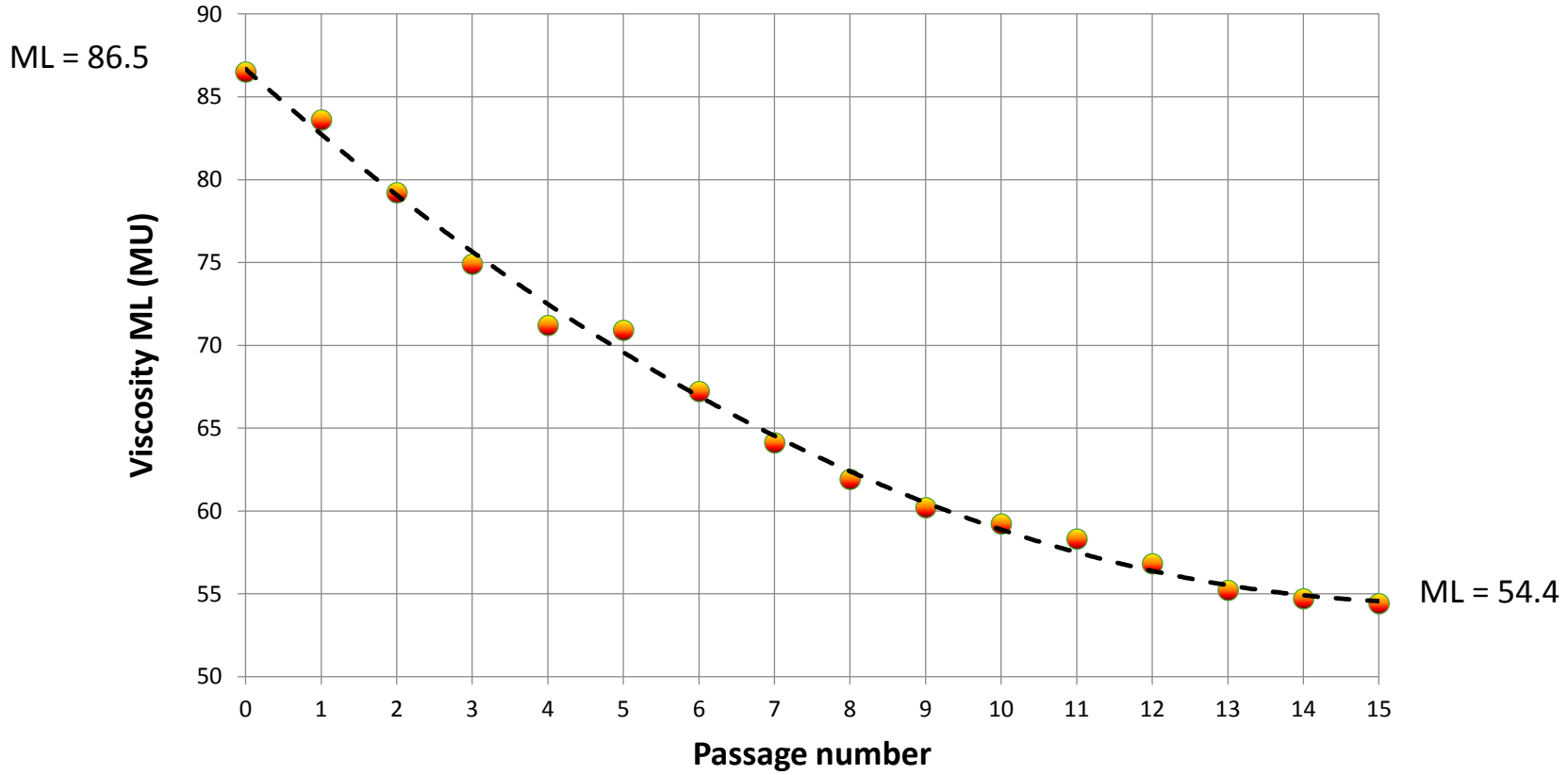
Structure and mechanical analysis




- Swelling rate (%)
- Soluble fraction (%)
- Mechanical characteristics (1 et 3)

# Evolution of dGTR characteristics over time

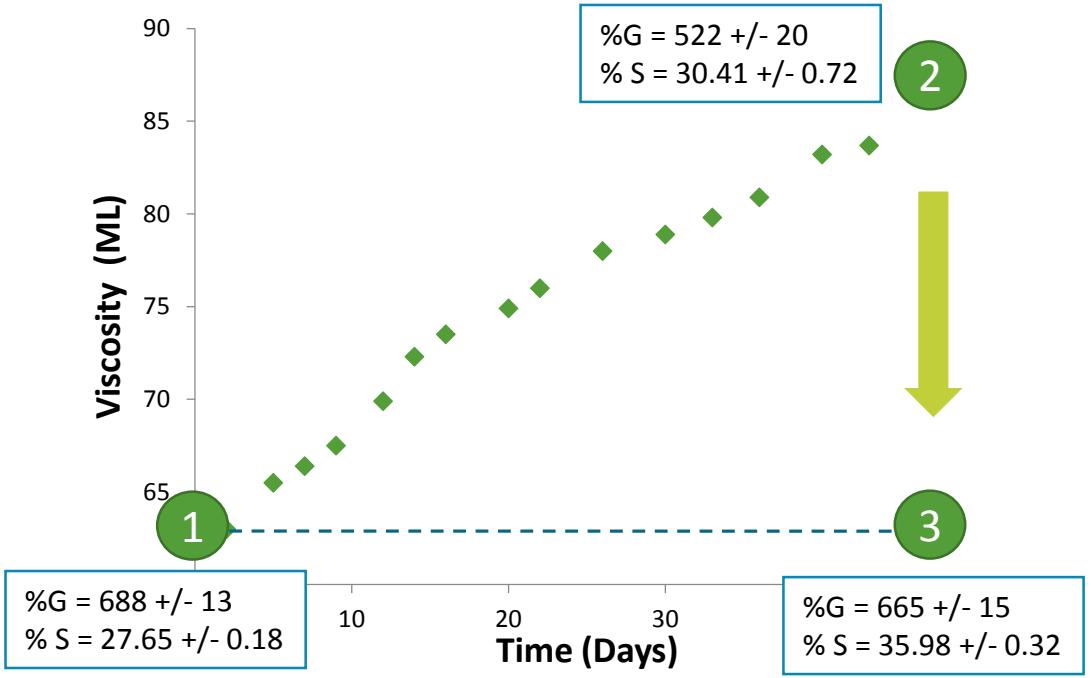
Evolution of the viscosity as a function of the number of passages in the twin roll mill (no friction)

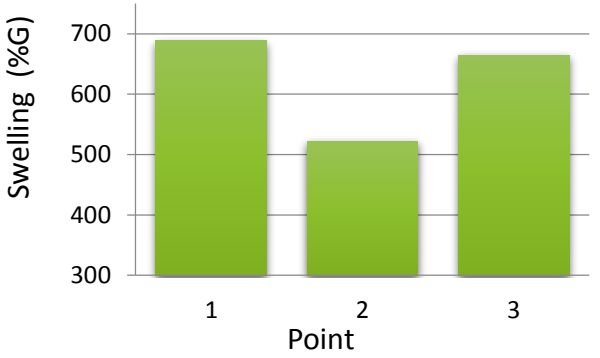


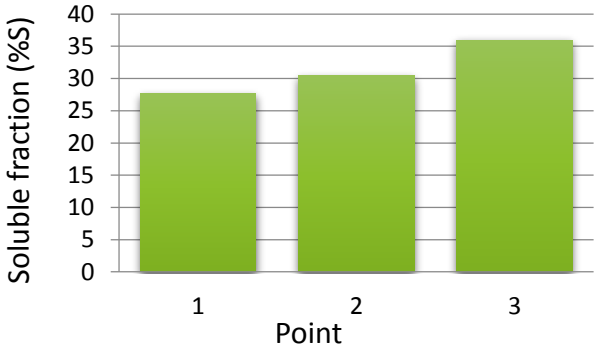

Initial viscosity = 62.3 ML; twin roll mill in calender function; gap = 5 mm

# Evolution of dGTR characteristics over time

Swelling and soluble fraction of dGTR before and after aging at ambient temperature



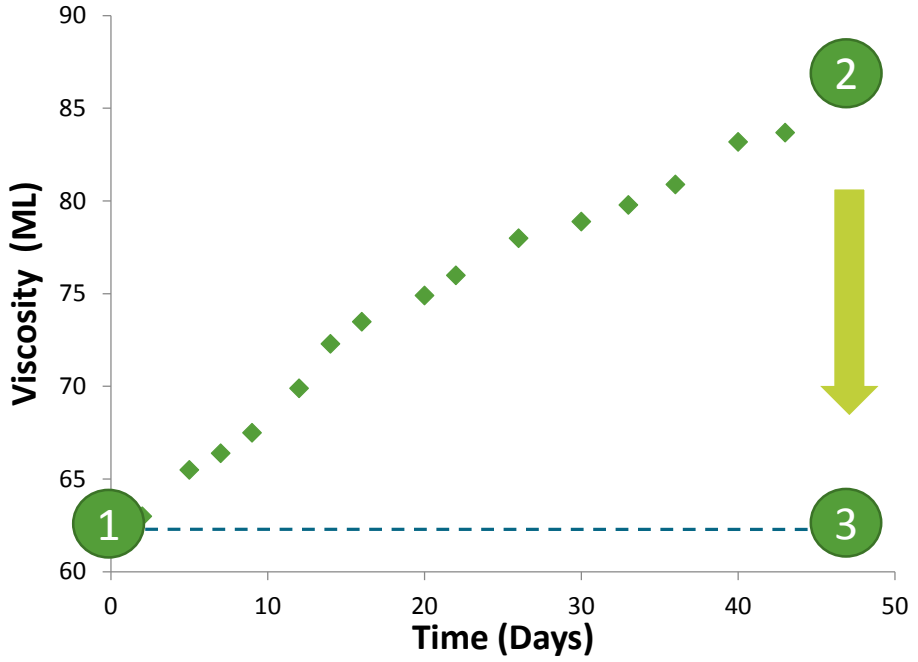




➢Decreasing of the swelling rate after aging (2) ➔ Reforming of the carbon black network limits the swelling rate.

➢Slight increase in soluble fraction ==> probable oxidation generating low molecular weights

# Evolution of dGTR characteristics over time

Mechanical characteristics of dGTR before and after aging



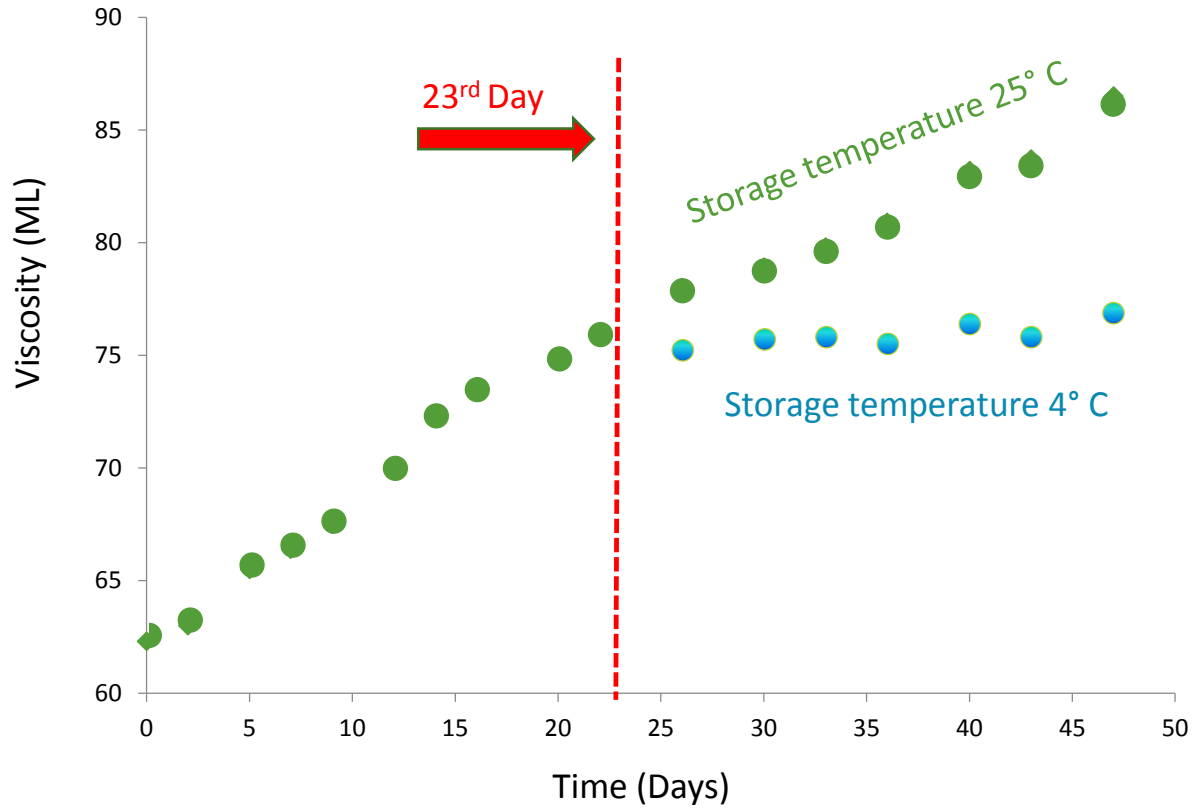

| | Tensile strength (Mpa) | | Strain at break (%) | |
|---|---|---|---|---|
| | Point 1 | Point 3 | Point 1 | Point 3 |
| With CO2sc | 16.25 | 15.43 | 322 | 285 |
| Without CO2sc | 15.42 | 14.94 | 332 | 272 |

| | Tensile strength (Mpa) | | Strain at break (%) | |
|---|---|---|---|---|
| | Point 1 | Point 3 | Point 1 | Point 3 |
| Without CO2sc / With 6PPD | 15.8 | 16.44 | 327 | 314 |

A slight deterioration of the mechanical characteristics of dGTR is observed (with and without CO2sc) ; this degradation is probably due to oxidation, which can be solved by the use of antioxidants.

# Evolution of dGTR characteristics over time

Stabilization of viscosity




The viscosity stabilizes and no longer evolves when the dGTR is stored at a low temperature

# Experienced issues

**Some problems remain and must be solved:**

- Smelling process and materials
- Obtaining a heterogeneous material (even more when the input materials are also (GTR-PC) )
- Difficult reuse in some sectors (medical and food industry..)

**→ Investigations are currently in progress**

# New developments

1. Collaboration with **Artis**

**Reinforcement of dGTR with rCB***
**for the production of « Super Green compounds »**

2. Collaboration with **ASTM** for determination of devulcanisates standards (Task group 11-20-01)

3. Collaboration with academic laboratories to solve issues concerning the smelling on certain rubbers

** r-CB: recovered CARBON BLACK produced by ELT's PYROLYSIS*

# Conclusion

Phénix can send you samples of rubber :

- Granulates
- Micronisates
- High-quality devulcanisates

and quotations for industrial units of these different technologies

*Even rubber scraps can have a second-life,*
*test our samples and let's talk about it !*