Damaging polyamide 6,6 with road salts

Renault Group

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Polyamide 6,6 in automotive context

Well-known materials for numerous plastic parts

- High mechanical resistance (E = 3 GPa, 85 MPa yield stress)
- Relatively high cristallinity rate: 40-50%

Targeted properties

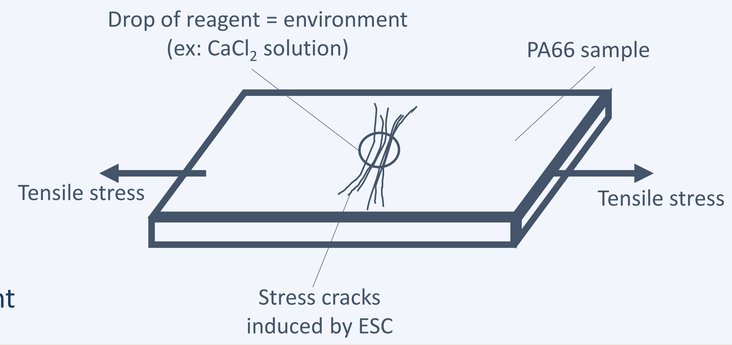
- High mechanical resistance
- Durability
- Recyclability
- Affordability

Drawbacks

- Hydrophilicity and swelling[1]
- Environmental stress cracking[2] (ESC):

Hypotheses on ESC mechanisms[3]

- Decrease in surface tension
- Plasticization and swelling caused by the environment



Project goal

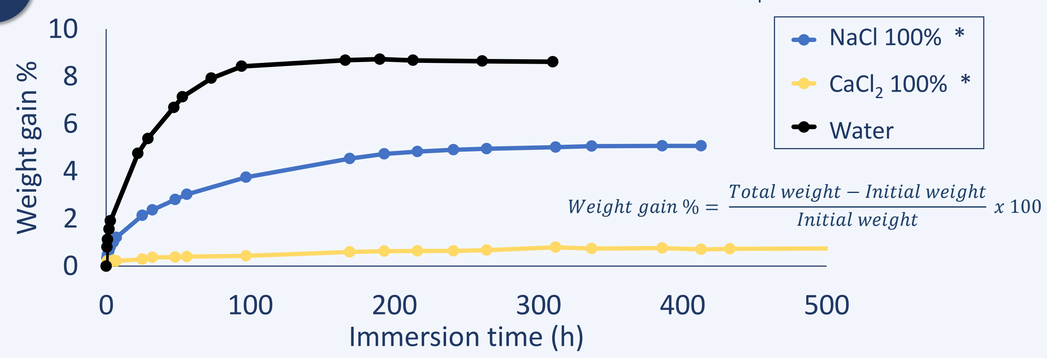
Understand the **damage mechanisms of PA 6,6** induced by solutions of selected metal salts (NaCl, $CaCl_2$)

Towards a better description of PA 6,6 environmental stress cracking mechanism

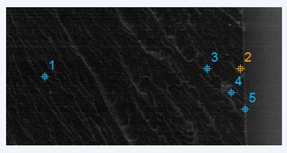
Reversible effects of NaCl and $CaCl_2$

1 *PA 6,6 immersion into salt solutions at 50°C*

→ 2mm-thick flat samples
→ 500µm-thick films



Cross-sectional SEM-EDX:



Atom Concentration %						
	C	N	O	Cl	Ca	Depth (µm)
Point 1	64.1	9.2	26.6			946
Point 2	66.2	9.2	23.4	0.3	0.1	13

→ Reversible water absorption during immersion into salt solutions without significant salt penetration

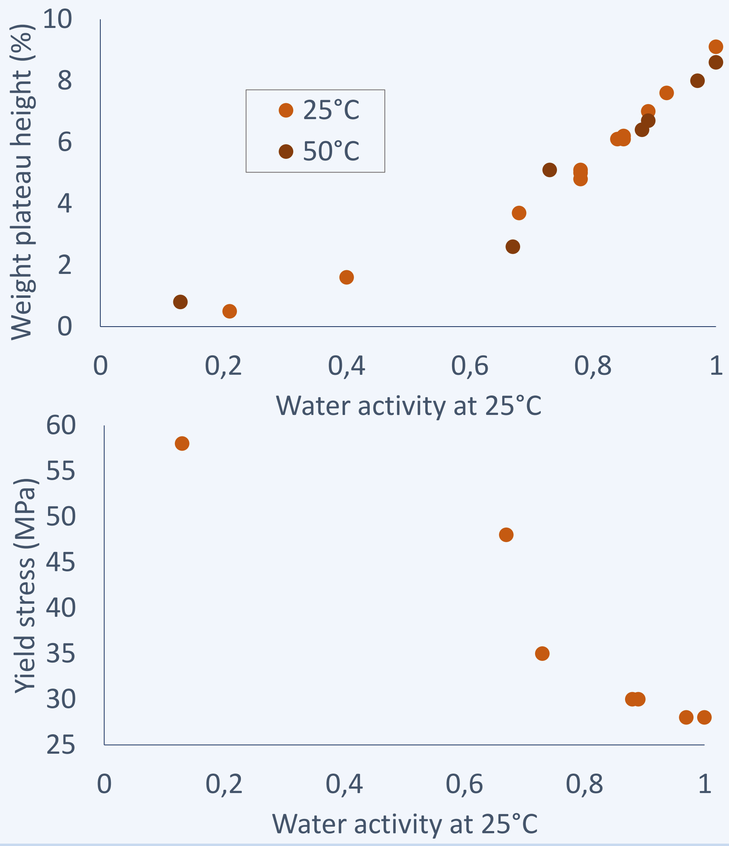
Cross-sectional µ-XRF:

Cl detection		
	Counts	Estimated concentration in mol/kg PA
NaCl	600	$< 10^{-4}$
$CaCl_2$	2500	<0.1

- **No significant permeability to NaCl or $CaCl_2$** (no chemical modification observed on IR spectra)
- **No crack propagation without applied stress**
- **Initial properties are recovered** after drying

*Concentrations are given in %vol. of saturated solutions at 50°C

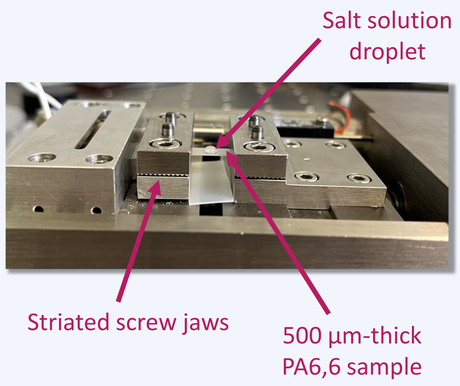
2 *Hypotheses: water activity induced phenomena*



Correlation between water activity and macroscopic effects, consistent with literature [4,5]

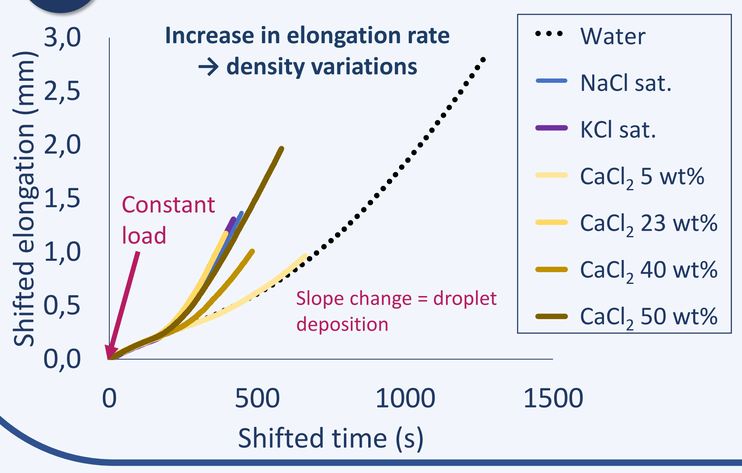
What are the impacts of applied stresses?

1 *Experimental set up and procedure*

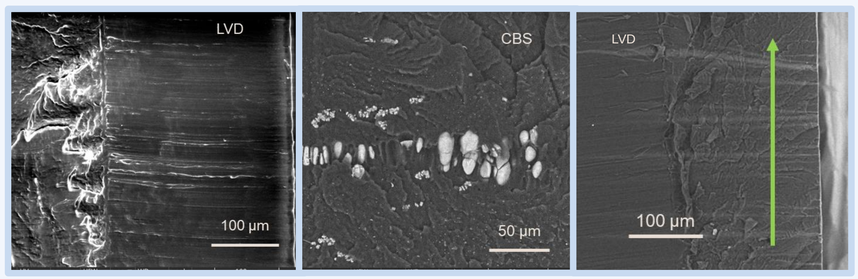


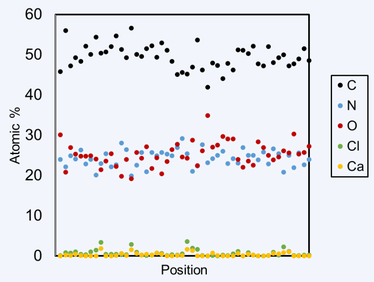
- Horizontal tensile testing
- 1.5 mm/min
- Pre-dried samples
- Constant force

2 *Elongation*



3 *Crazing phenomena at yield stress*



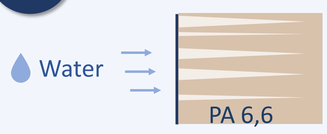


EDX line scan

Cross-sectional SEM after contact with:

Water	NaCl 25wt%	$CaCl_2$ 35wt%
Surface wrinkles, porosity?	**Surface wrinkles, porosity, salt crystals**	**Surface wrinkles, porosity?, embedded ions, large contrasting zones**

4 *Hypotheses on the cracking mechanisms*



Plasticization
→ "Soft" zones confined between "hard" zones

2 competing phenomena: Necking vs Cavitation

Water and NaCl

Water

Plasticization effect
+
Potential osmotic pressure or surface tension effects

$CaCl_2$

Ion complexation
↓
Stabilization effect

Next steps

- Symmetrical contact under stress : tensile testing during immersion
- Study on chemical interactions for the considered ions

Conclusions

- Without applied stress, the observed behaviors are only related to the tuning of the water activities by the different salts
- Significant applied stress seems necessary to generate stress cracking on PA 6,6 films inducing 2 different types of behavior
- The effects of ions seem mainly related to their chemical affinity with the PA matrix

[1] Puffr and Sebenda, J.Polym.Sci. , Polym. Symp. **1967**
[2] Dunn and Samson, J.Appl.Polym.Sci. **1969**
[3] Robeson, Polym. Eng. Sci **2013**
[4] Labuza et al., Journal of Food science **1985**
[5] Reuvers et al., Polymer **2013**