POLYCARBONATE DIOL-BASED POLYURETHANE SEALANTS WITH IMPROVED WEATHERING AND CHEMICAL RESISTANCE INTENDED FOR BUILDING AND CONSTRUCTION

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Outline

- ✓ Introduction
- ✓ Experimental
- ✓ Results and discussion
- ✓ Conclusions

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Requirement of sealants for construction

- ✓ Good damping properties
- ✓ Appropriate flexibility and toughness
- ✓ Good adhesion to different substrates
- ✓ Excellent weathering resistance

Common sealants for construction

- ✓ Asphalt and bitumens
- ✓ Silicones
- ✓ Polyurethanes

Benefits of PU sealants

- ✓ Excellent stress recovery
- ✓ Fast curing rate
- ✓ High adhesion to non-primed substrates
- ✓ Good surface energy (paintable)
- ✓ Rapid initial adhesion (green strength)

PU sealants are used in broad range of applications

Building and construction - Pavement joints, wall gaps

PU sealants are used in broad range of applications

Civil Engineering - Railway beds, cracks/grooves in roads

Raw materials for PU sealants

- ✓ Polyols
  - ✓ Polyether
  - ✓ Polyester
  - ✓ Polycarbonate diol
- ✓ Isocyanates
- ✓ Chain extender
- ✓ Additives and fillers

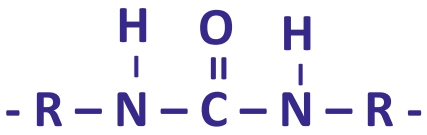
One-component PU sealants

OCN – R – NCO

NCO-terminated prepolymer

$+H_2O$
$-CO_2$

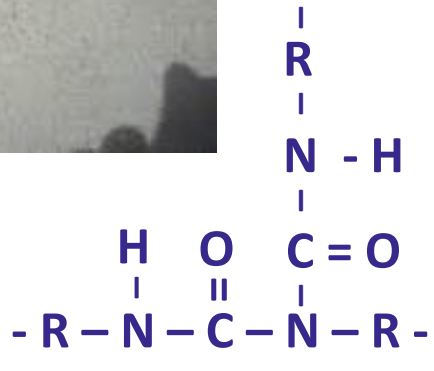
MOISTURE CURE



Urea group

- R - NCO

CROSS-LINKING



Biuret

Two-component PU sealants

Component A

Polyfunctional diols and/or diamines

$HO - R - OH$

$H_2N - R' - NH_2$

+

MIXING

↓

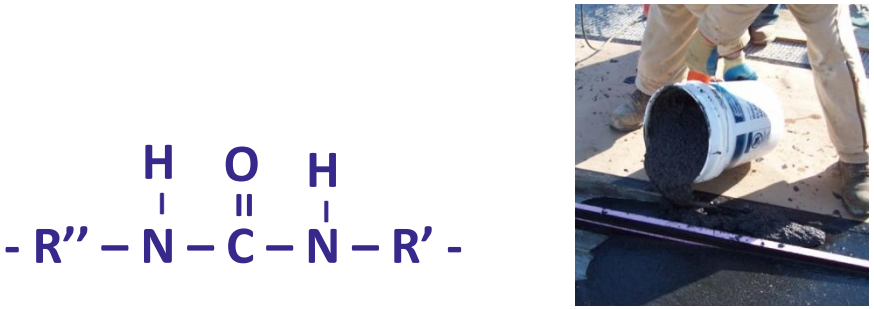
Urethane

Component B

Polyisocyanate or NCO-terminated prepolymer

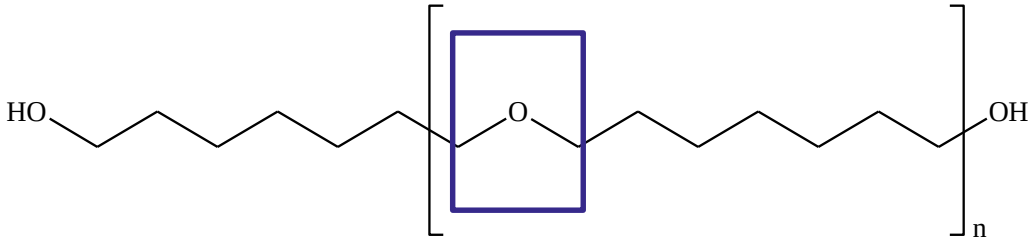
$OCN - R'' - NCO$

↓

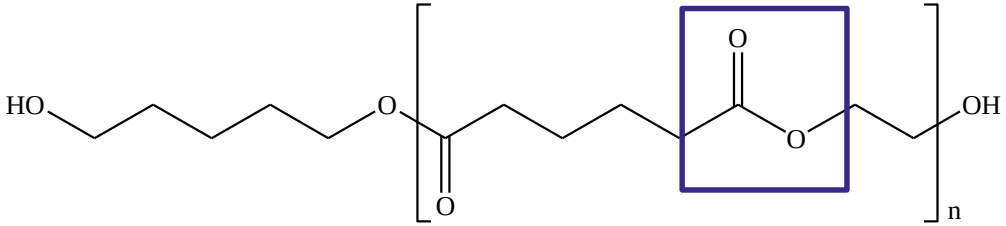


Urea

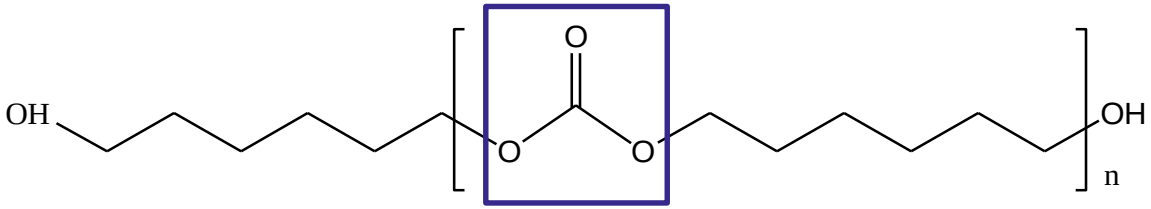
Polyol nature



POLYETHER



POLYESTER



POLYCARBONATE

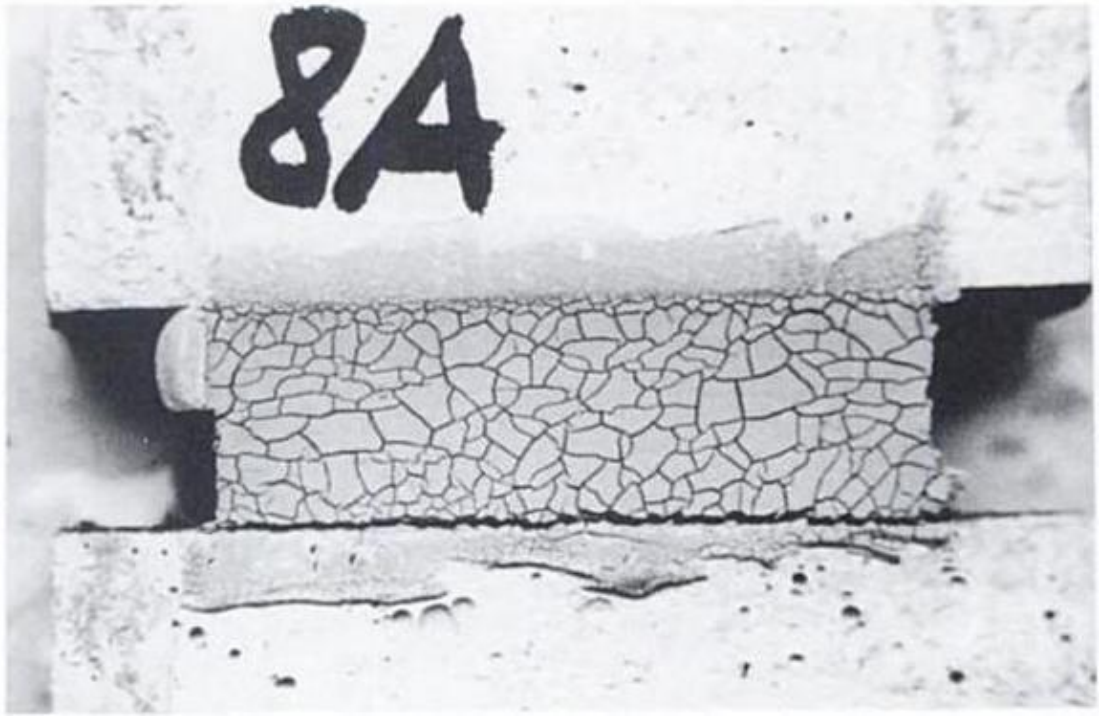
Polyol nature

Polyurethane property	Polyether	Polyester	Polycarbonate diol
Hydrolitic stability	YES	NO	YES
Resistance to solvents	NO	YES	YES
Thermal stability	NO	YES	YES
Chemical resistance	YES	NO	YES
Damping	YES	NO	YES
Mechanical properties	NO	YES	YES

Current limitations of PU sealants

Most of currently commercial PU sealants based on polyether/polyester polyols show limited resistance against ageing

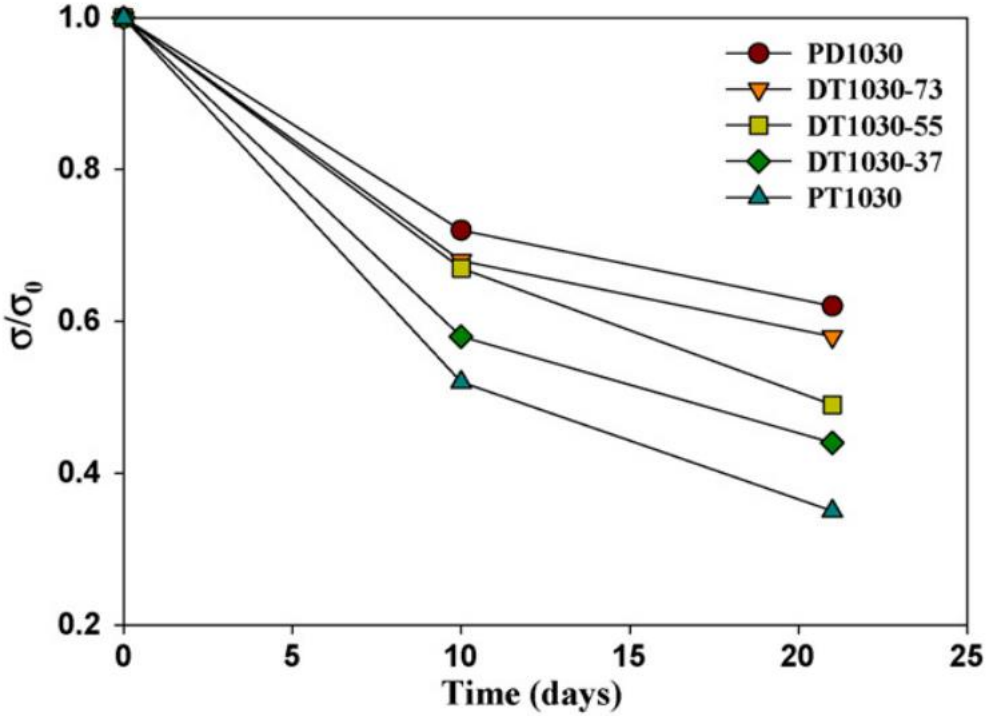
Current limitations of PU sealants



- ✓ Cracking
- ✓ Swelling
- ✓ Yellowness
- ✓ Softening
- ✓ Debonding

J.C. Beech, A.T. Woolf. *Durability of Building Sealants.* Routledge (Taylor & Francis), London, UK (2013). ISBN: 9781136743603. Chapter 6: *Ageing resistance of building and construction sealants (Part I). pp. 63 – 90.*

How to improve the ageing of PU sealants?



Higher content of ester groups in polyurethane structure inhibited the loss of the mechanical properties after hydrolitic degradation

S.H. Park, I.D. Chung, A. Hartwig, B.K. Kim. *Hydrolytic stability and physical properties of waterborne polyurethane based on hydrolytically stable polyol.* Colloids and Surfaces A. Physicochemical and Engineering Aspects **305(1-3)**, 126 – 131 (2007).

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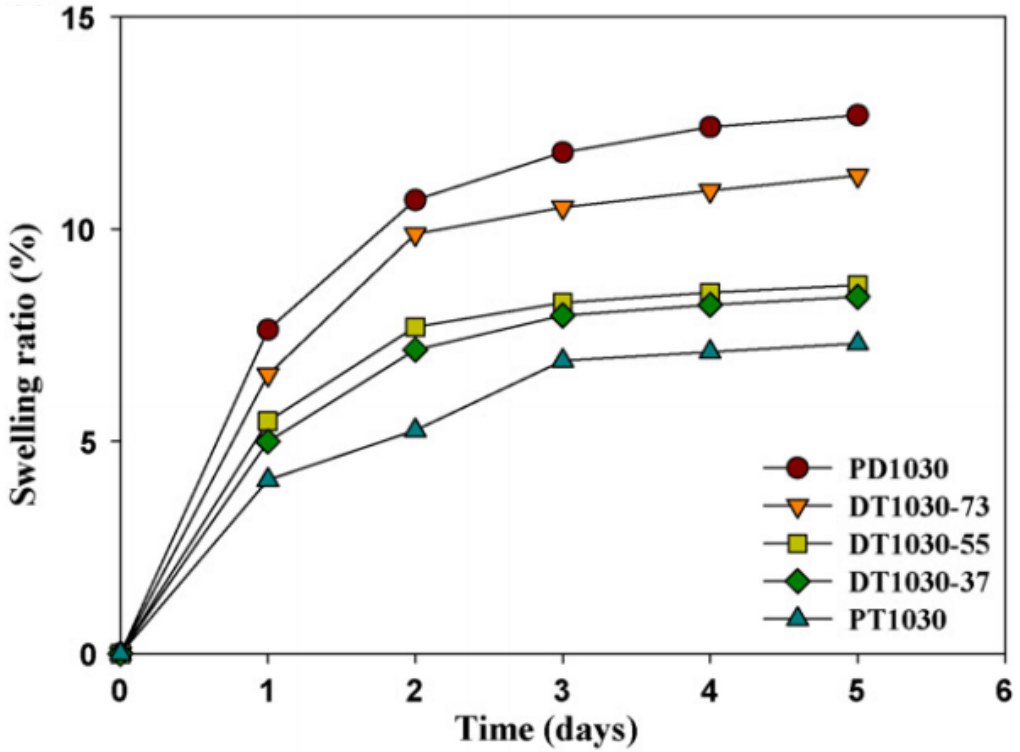

Higher content of ester groups in polyurethane structure increased the swelling resistance in hot water of the PU sealant

S.H. Park, I.D. Chung, A. Hartwig, B.K. Kim. *Hydrolytic stability and physical properties of waterborne polyurethane based on hydrolytically stable polyol.* Colloids and Surfaces A. Physicochemical and Engineering Aspects **305(1-3)**, 126 – 131 (2007).

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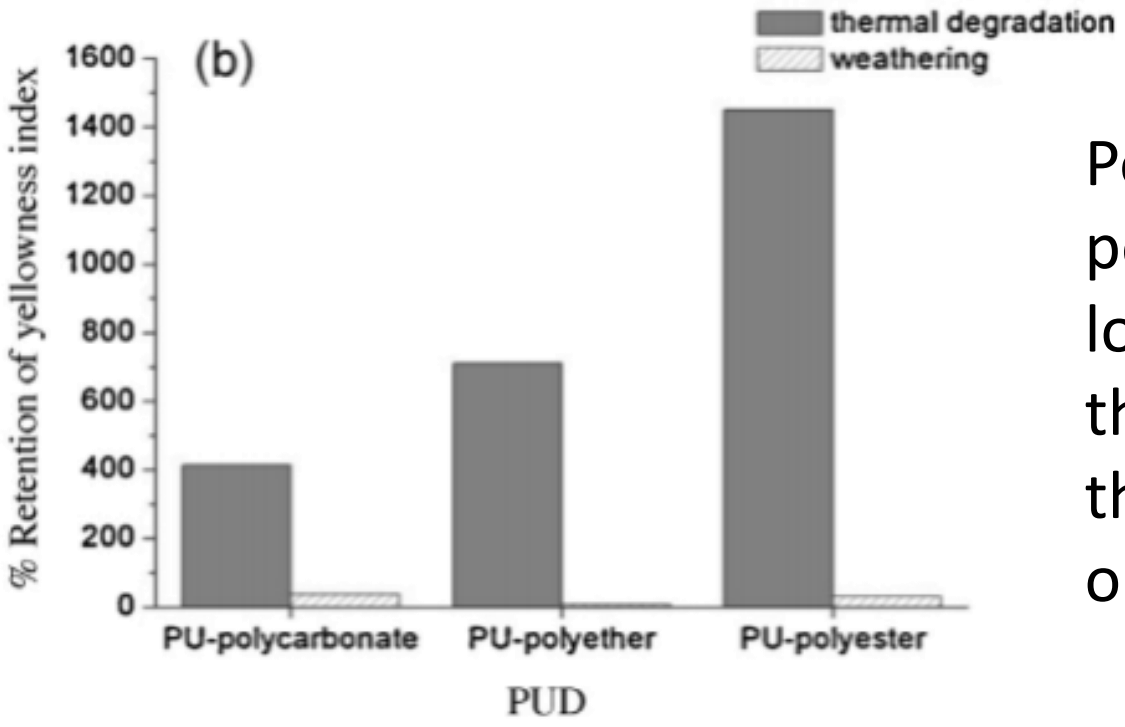

Polyurethanes made with polycarbonate diol showed lower yellowness after thermal degradation than those made with polyether or polyester

V. García-Pacios, M. Colera, Y. Iwata, J.M. Martín-Martínez. *Incidence of the polyol nature in waterborne polyurethane dispersions an their performance as coatings on stainless steel*. Progress in Organic Coatings **76(12)**, 1736 – 1729 (2013).

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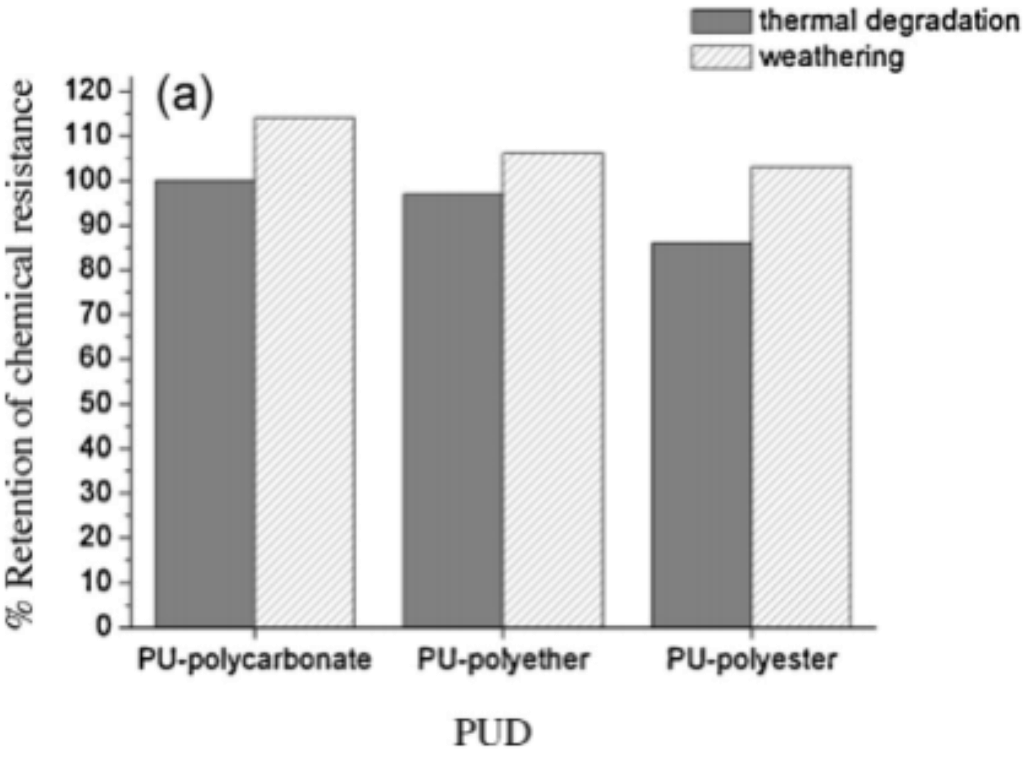

Polyurethanes made with polycarbonate diol showed higher retention of chemical resistance both after thermal degradation and upon weathering

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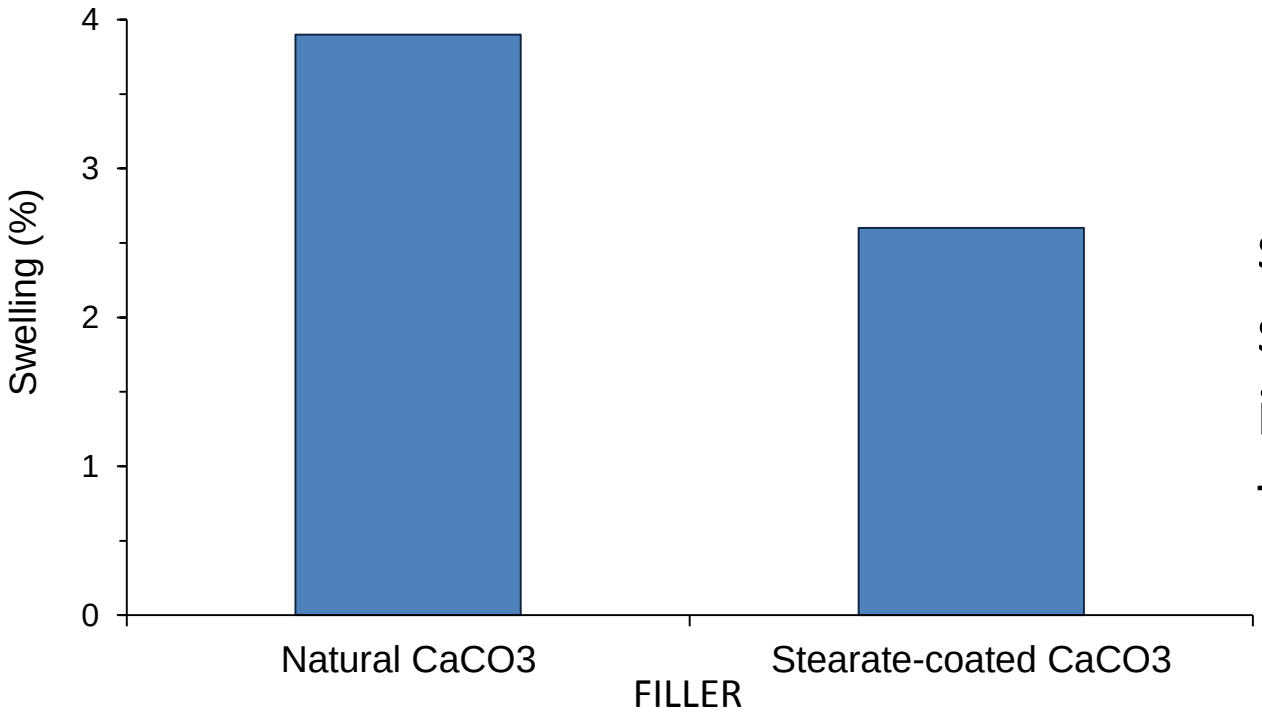

Resistance to swelling of PU sealants was improved by adding fillers

M.Y.L. Chew. *The effects of some chemical components of polyurethane sealants on their resistance against hot water.* Building and Environment **38(12)**, 1381 – 1384 (2003).

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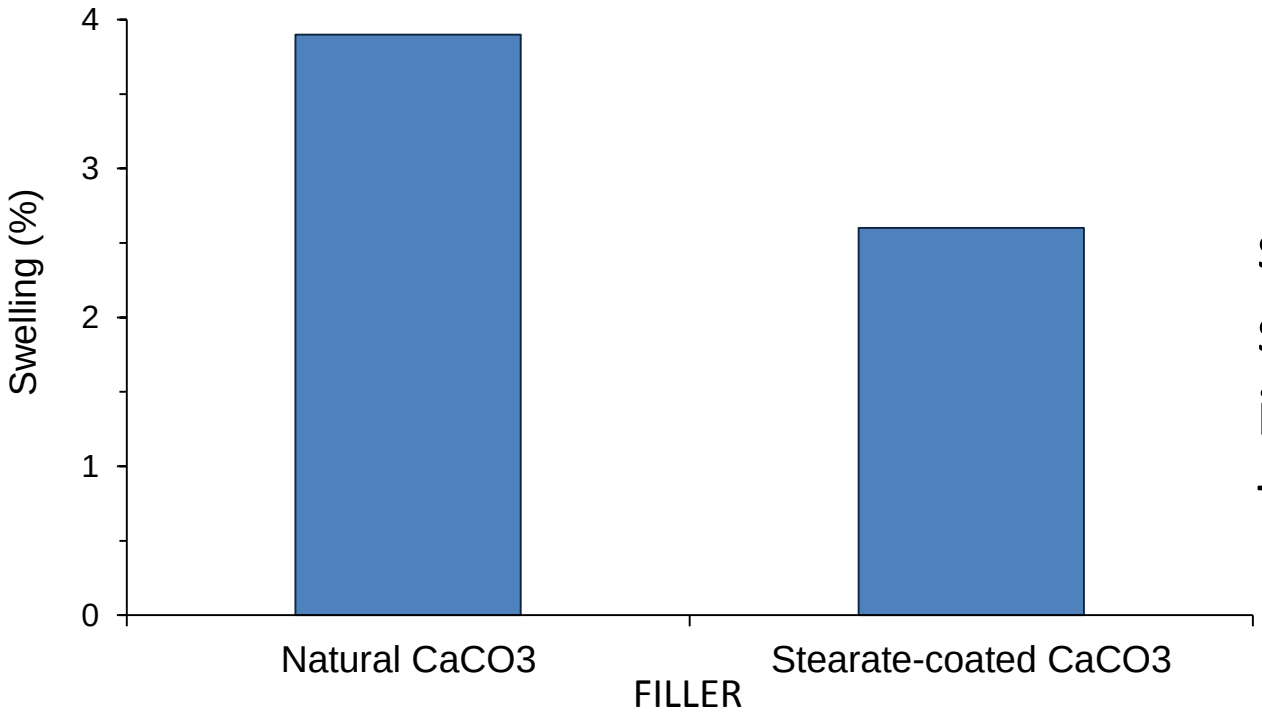

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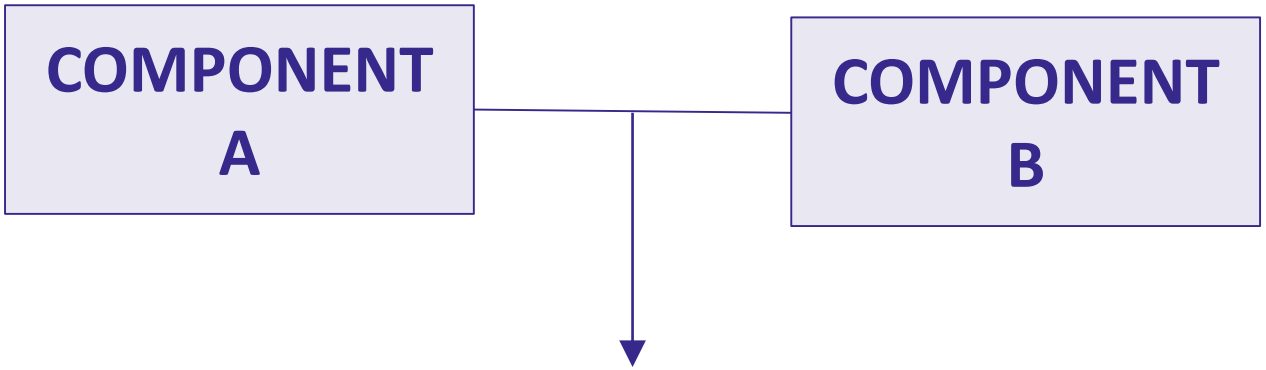
Materials

Polyether/polyester-based PU sealant	New PU sealant made with polycarbonate diol
Commercial benchmark	✓ ETERNACOLL® polycarbonate diol ✓ Polymeric MDI (Suprasec® 2445) ✓ Chain extender: 1,4-butanediol ✓ Catalyst: DBTDL (0.05 wt%) ✓ NCO/OH = 1.1

Materials

Two-component PU sealants made with PCD



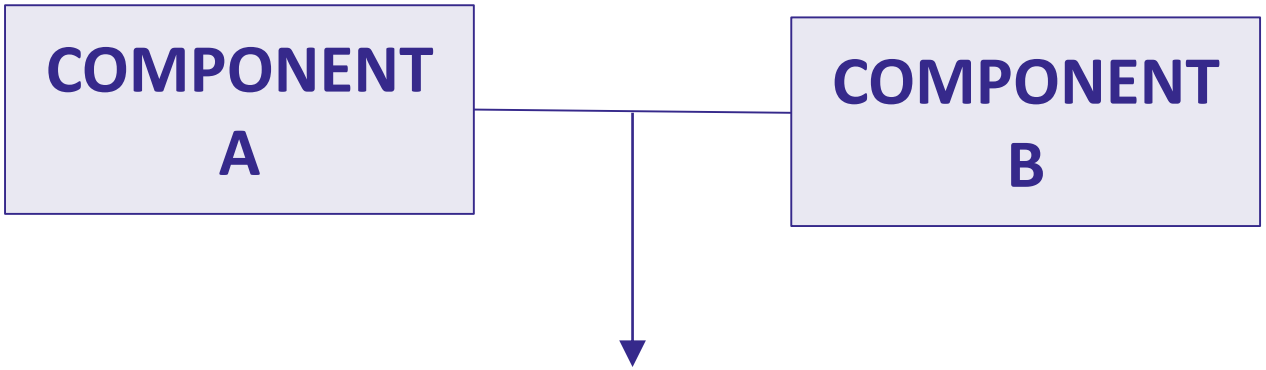
Stirring at 2500 rpm for 1-2 minutes

+

Curing at 25ºC for 24h

Materials

Two-component PU sealants made with PCD



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Experimental techniques

- ✓ **Stress-strain tests (ISO 37:2005)**
  Instron 4411, Instron Corp. (Norwood MA, USA)

- ✓ **Thermal gravimetric analysis**
  Q500, TA Instruments. (New Castle DE, USA)

- ✓ **Differential Scanning Calorimetry**
  Q100, TA Instruments. (New Castle DE, USA)

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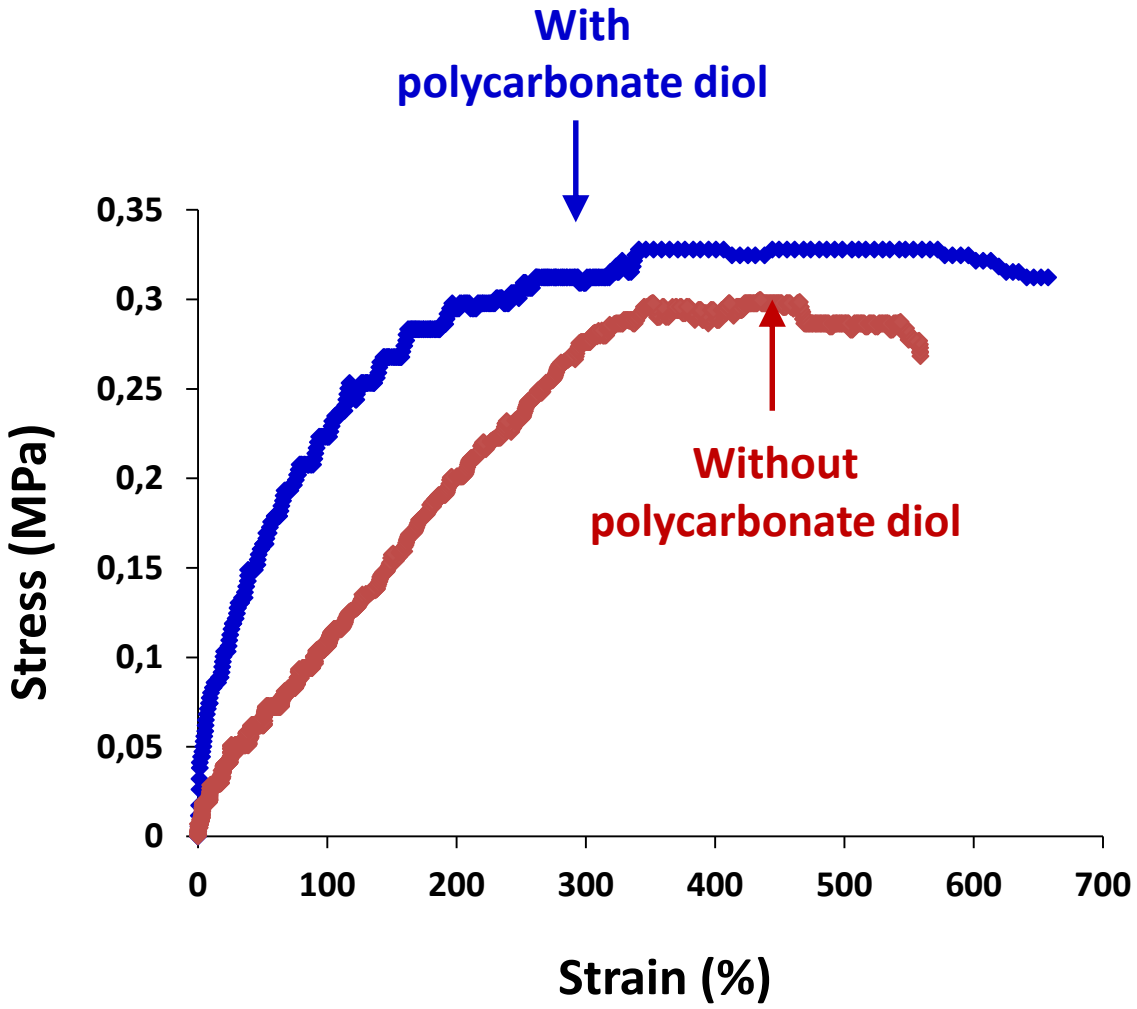


Stress-strain

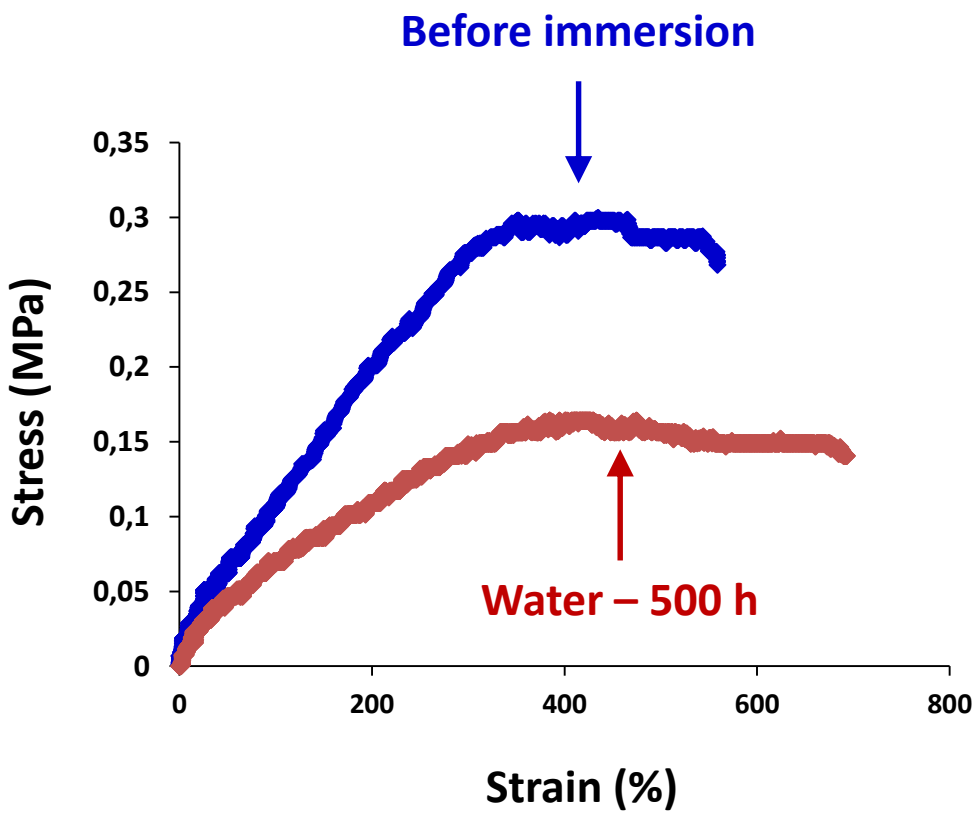
PU sealant made with polycarbonate diol shows similar performance than commercial polyether/polyester -based sealant

Stress-strain

PROPERTY	BENCHMARK	PCD-based PU
Tensile strength (MPa)	0.30	0.33
Elongation-at-break (%)	>500	>500
Young's modulus (MPa)	0.22	0.29
Toughness (kJ/m^3)	825	1882
Hardness (ºShore A)	20	15

Immersion in water

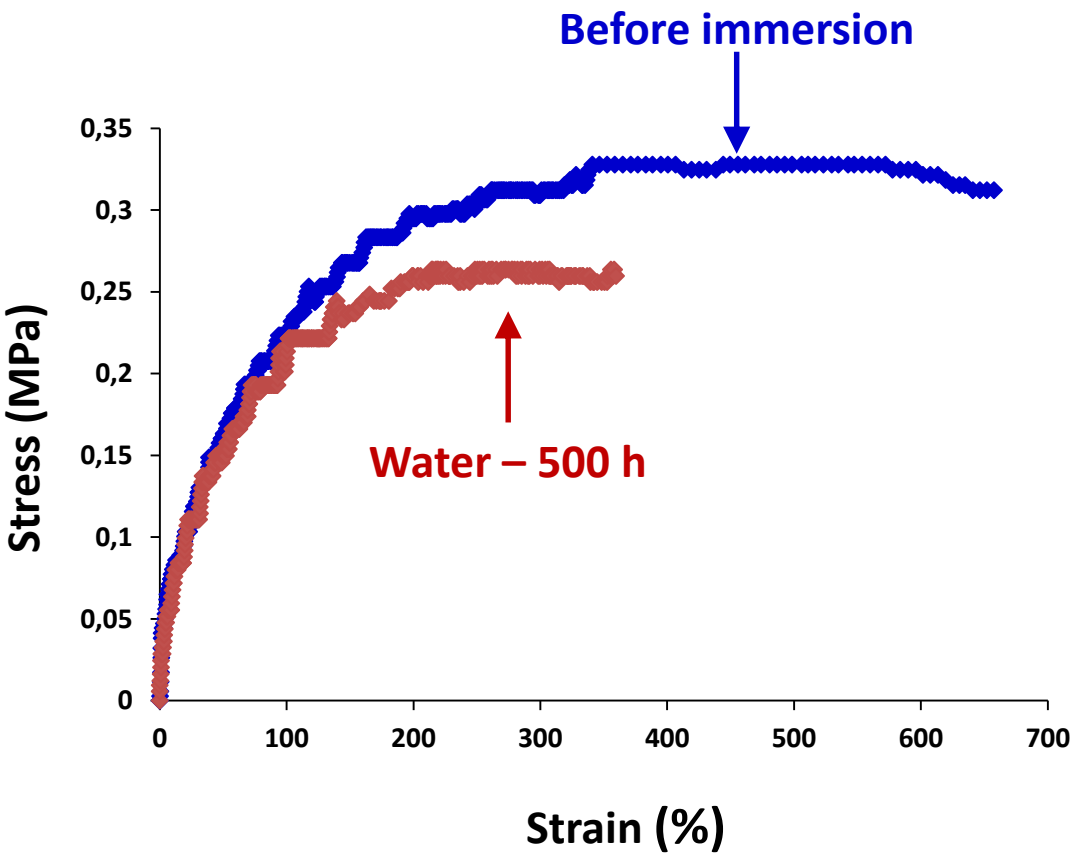
Stress-strain



Commercial polyether/polyester -based sealant losses 45% tensile strength property by immersion in water

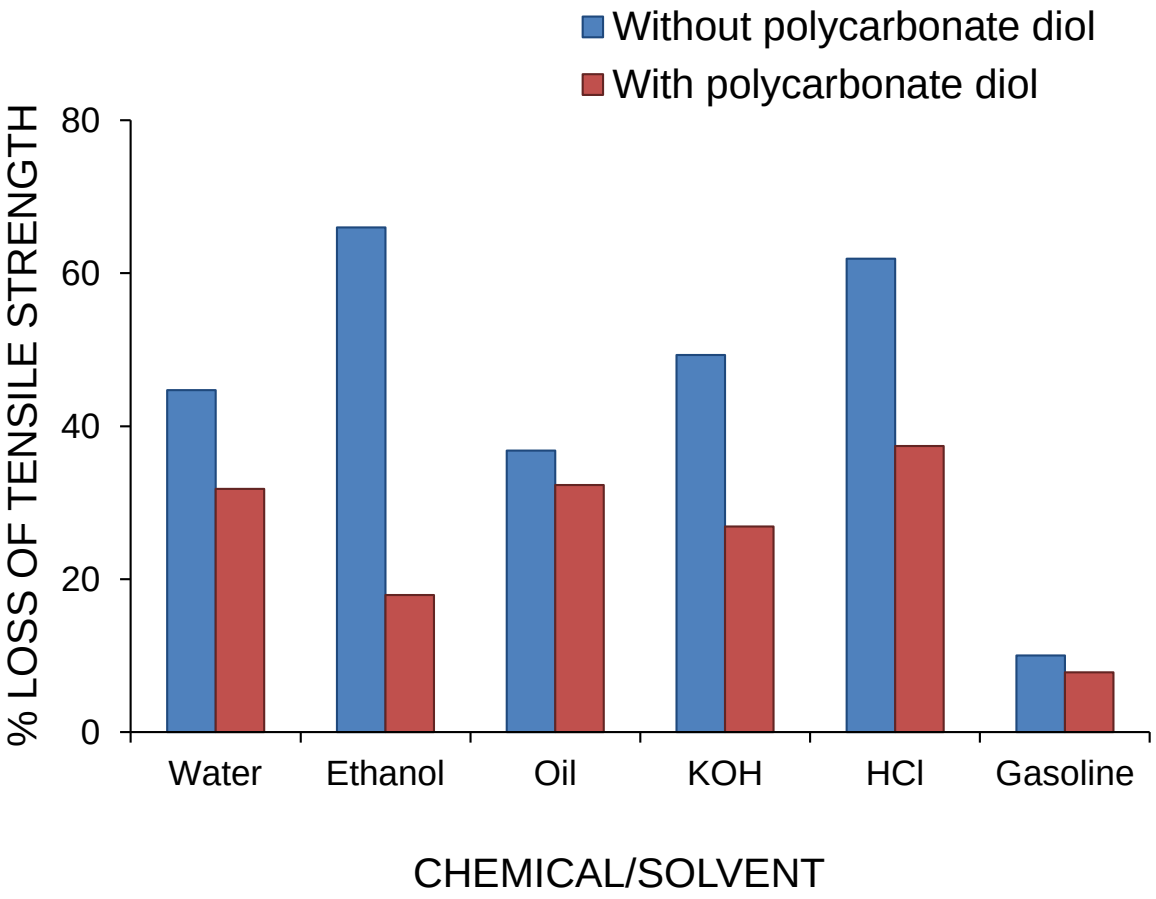
Immersion in water

Stress-strain



PU sealant made with polycarbonate diol losses 22% tensile strength property by immersion in water

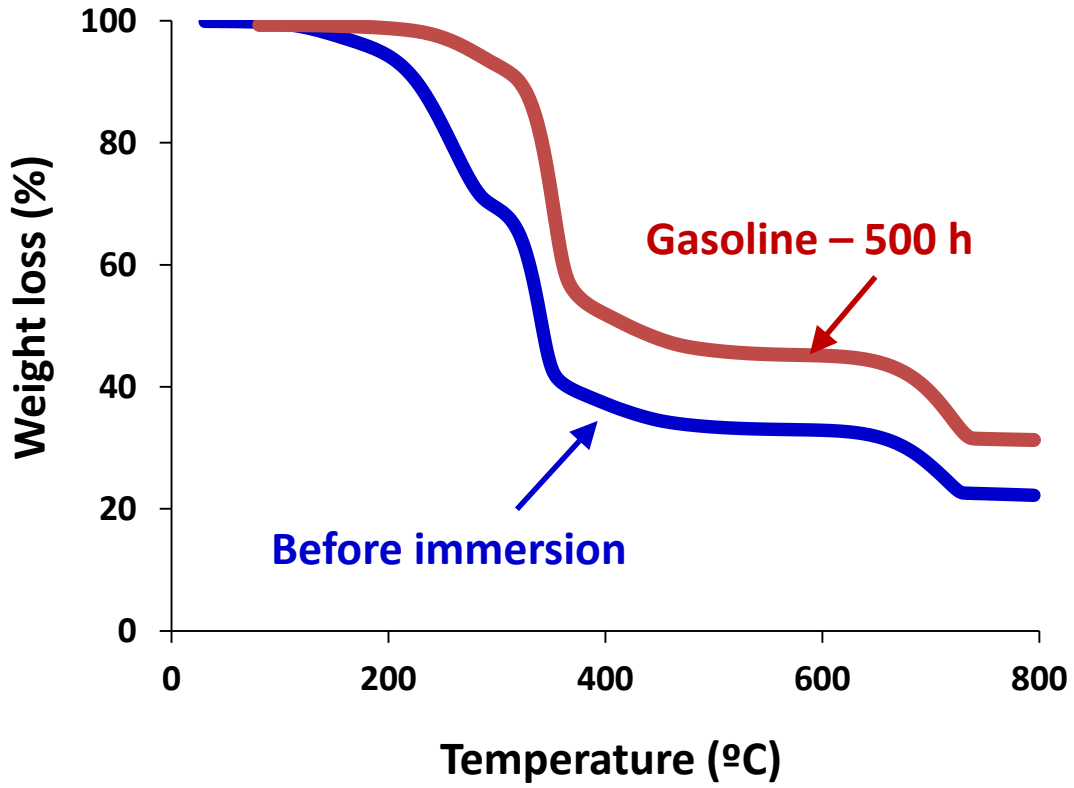
Stress-strain



Immersion in different chemical/solvents for 3 weeks at 25ºC

Immersion in gasoline

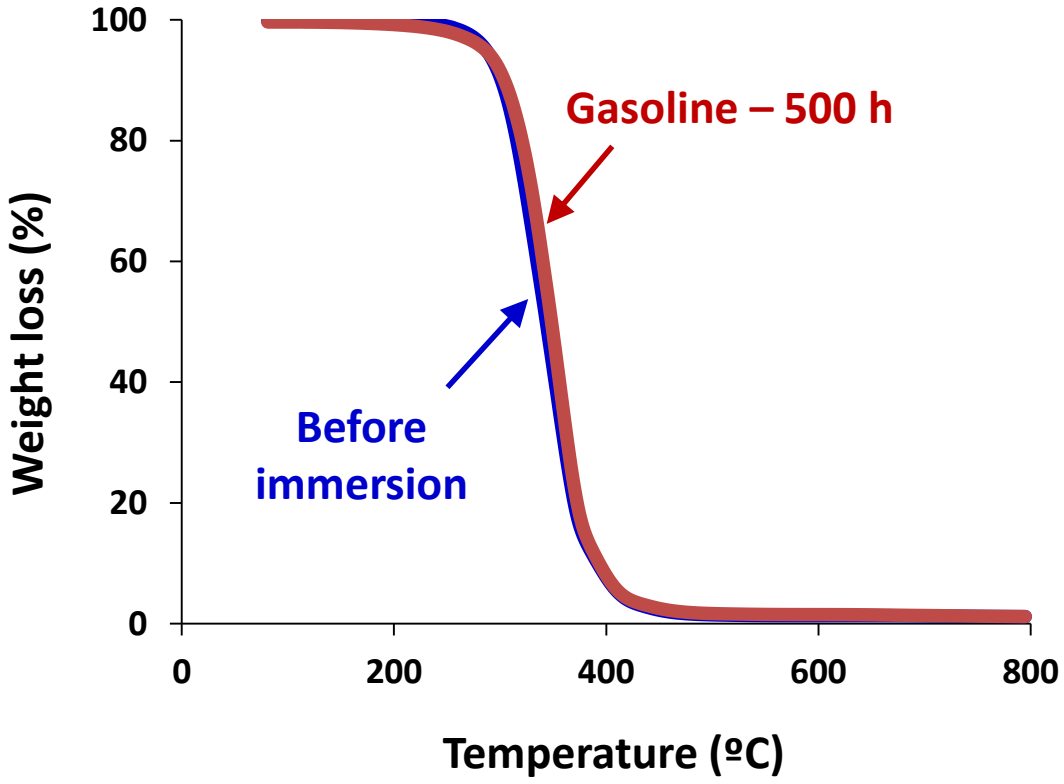
TGA



Structure of commercial polyether/polyester-based sealant is altered by immersion in gasoline

Immersion in gasoline

TGA



Thermal stability of PU sealant made with polycarbonate diol Eternacoll® doesn't change after immersion in gasoline

Effect on molecular structure

DSC

Liquid	Tg (ºC)	
	Without PCD	With PCD
Pristine	-42	-41
Water (25ºC)	-35	-41
Gasoline	-28	-41

Glass transition temperature of PU sealant made with polycarbonate diol Eternacoll® doesn't change after immersion in different fluids

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- **PU sealants made with Eternacoll® polycarbonate diol showed good mechanical performance after immersion in different solvents/chemicals**

- **Polyurethane sealants made with Eternacoll® polycarbonate diol improved the resistance to hydrolysis and degradation in solvents/chemicals**

THANK YOU FOR YOUR ATTENTION!!

Willing to improve the performance of your polyurethanes? Wanting to know more about ETERNACOLL® polycarbonate diols and ETERNATHANE ® prepolymers?:

- ✓ ***Google "UBE polycarbonate diol" and visit our website.***
- ✓ ***Write me an e-mail to m.colera@ube.es***