NOVEL POLYURETHANE COATINGS OBTAINED WITH POLYCARBONATE DIOL FOR PIPELINES WITH IMPROVED MECHANICAL PROPERTIES AND HYDROLYSIS RESISTANCE

J.A. Jofre-Reche, A.J. Yáñez-Pacios, M. Fuensanta, O. Coloma-Esteban, J.M. Martín-Martínez

University of Alicante (Spain)

F. Rodríguez-Llansola, M. Colera, A. Nohales, I. Iglesias, V. Costa

UBE Corporation Europe, S.A.U (Spain)

- Introduction
- Experimental
- Results and discussion
- Conclusions

- **Introduction**
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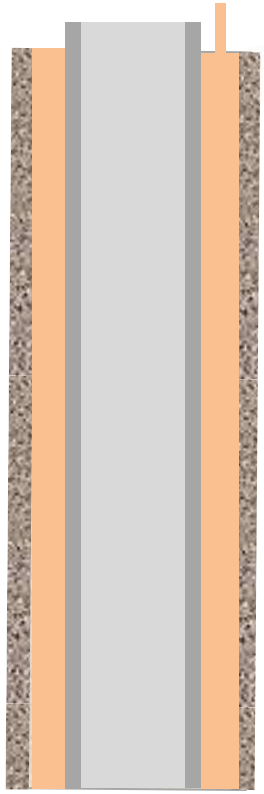
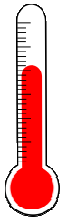
- **Internal polyurethane coatings of pipelines for improving abrasion resistance**

- **Current coating : Polyether-based polyurethane**

Actual manufacturer procedure →





= 80ºC

- **Polyurethane coatings improved wear resistance of pipelines.**

R.J.K. Wood, Y, Puget, K.R.Trethewey, K. Stokes. ***«The performance of marine coatings and pipe materials under fluid-borne sand erosion»*** Wear 219, 46-59 (1998)

- **Fillers and additives have been used to improve abrasion resistance of polyether and polyester-based polyurethane coatings**

S. Zhou, L. Wu, J. Sun, W. Shen. ***«Effect of nanosilica on the properties of polyester-based polyurethane»*** Journal of Applied Polymer Science 88 (1), 189-193 (2003)

H. Song, Z. Zhang, X. Men, Z. Luo. ***«A study of the tribological behavior of nano-ZnO-filled polyurethane composite coatings»*** Wear 269 (1-2), 79-85 (2010)

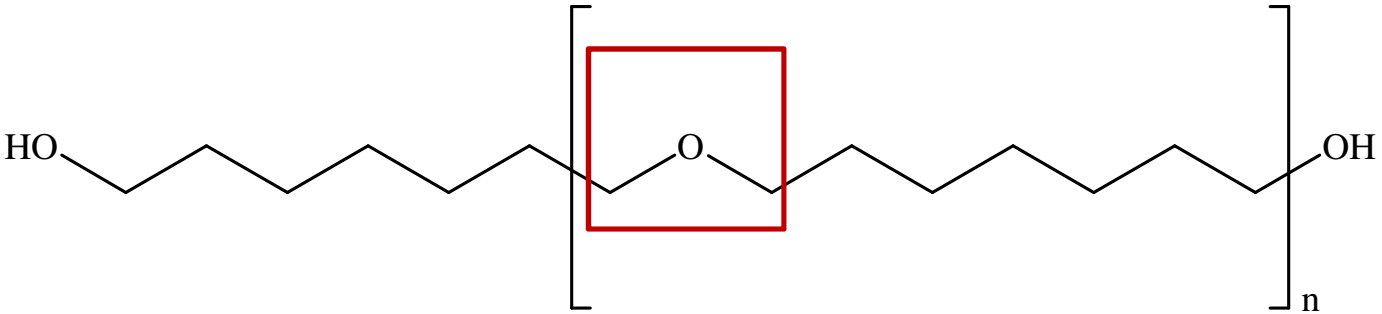
➡ Current drawbacks and limitations of PU as pipeline coating

- ✓ Limited hydrolytic stability and chemical resistance
- ✓ Additives for abrasion improvement are expensive
- ✓ Frequent maintenance

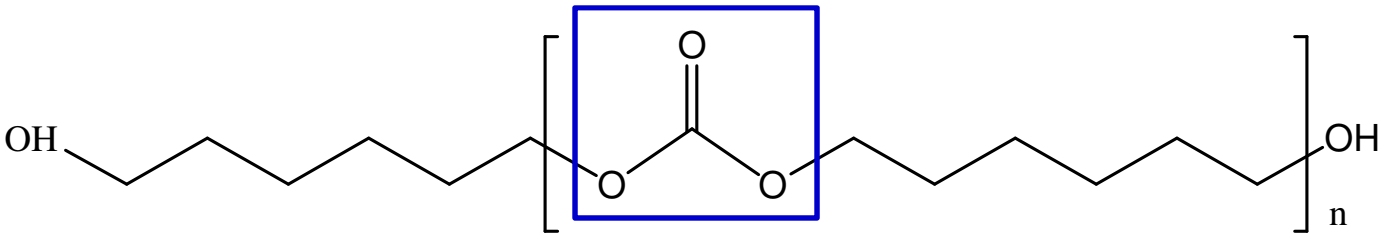
- **Improved ageing resistance and adhesion have been shown in polycarbonate diol-based polyurethanes compared to polyether and polyester-based polyurethanes.**

V. García-Pacios, M. Colera, Y. Iwata, J.M. Martín-Martínez. ***«Incidence of the polyol nature in waterborne polyurethane dispersions on their performance as coatings as stainless steel»*** Progress in Organic Coatings 276 (12), 1726-1729 (2013)

Polyether



Polycarbonate diol



Advantages of polycarbonate diols:

- ✓ Good durability
- ✓ Good properties at low temperature
- ✓ High chemical resistance
- ✓ High thermal stability
- ✓ High mechanical properties
- ✓ Excellent hydrolytic stability

➡ *Objectives*

- ❑ Improving mechanical properties and abrasion resistance of PU coatings
- ❑ Improving durability of internal PU coatings for pipelines

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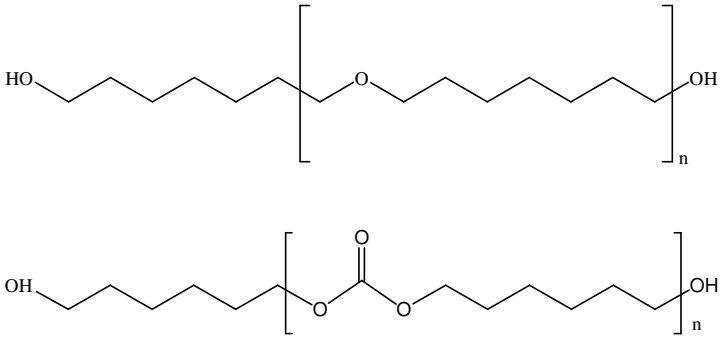
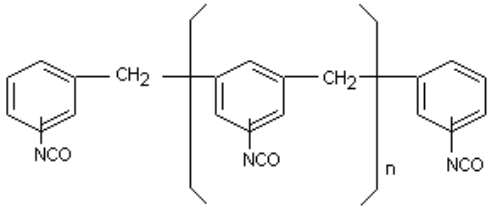
SYNTHESIS OF PUs - OUR STRATEGY

➡ Polyurethane coatings («one shot» process):





Polyether diol + polycarbonate diol | **Polymeric MDI** | **1,4-butanediol**

POLYURETHANE

RAW MATERIALS

➡ **Polyols**
- Polyether: Polytetramethyleneglycol (PTMEG)
- Polycarbonate diol MW = 500

Polytetramethyleneglycol
PTMEG
M_w = 1000 Da

Eternacoll® polycarbonate diol
M_w = 500 Da

RAW MATERIALS

- Isocyanate: Polymeric MDI (pMDI)
- Chain extender: 1,4-butanediol

EXPERIMENTAL TECHNIQUES

- **Thermal gravimetric analysis**

Thermal properties were measured using thermal gravimetric analysis (TGA) in TGA system by heating from room temperature to 800ºC at 10ºC/min under nitrogen atmosphere

EXPERIMENTAL TECHNIQUES

- **Differencial Scanning Calorimetry**

The structure of the polyurethanes was analyzed by differential scanning calorimetry (DSC) using DSC system by heating from -70ºC to 100ºC at 10ºC/min under nitrogen atmosphere followed by cooling down to -70ºC and carrying out a second heating from -70ºC to 100ºC at 10ºC/min.

EXPERIMENTAL TECHNIQUES

- **Wear resistance- ASTM D4060**

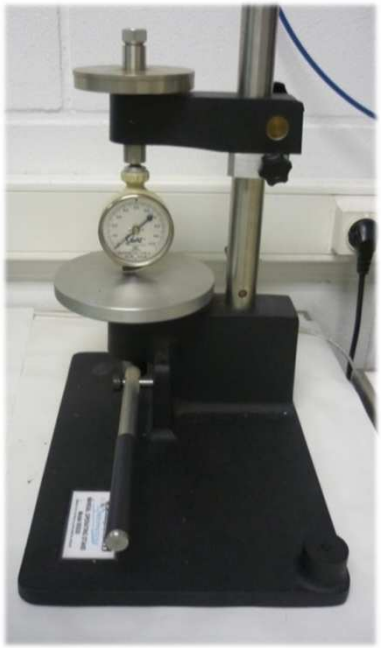
Abrasion resistance was evaluated using rotational abrameter with an abrasive wheel according to ISO 54701 standard.

EXPERIMENTAL TECHNIQUES

- **Optical microscopy**

EXPERIMENTAL TECHNIQUES

- **Shore A hardness: ISO 868:2003**



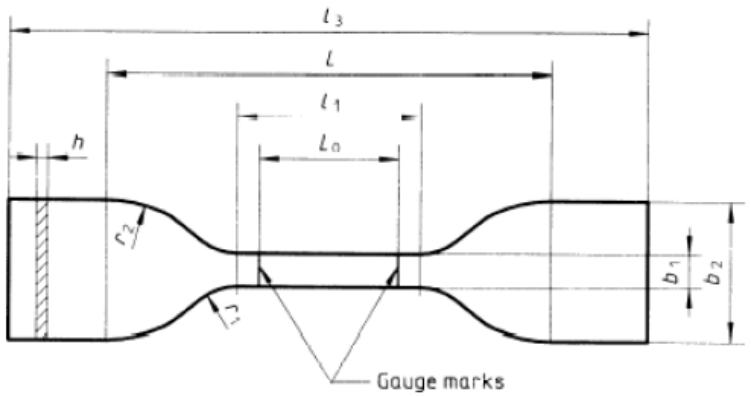
EXPERIMENTAL TECHNIQUES

- **Mechanical properties**

EXPERIMENTAL TECHNIQUES

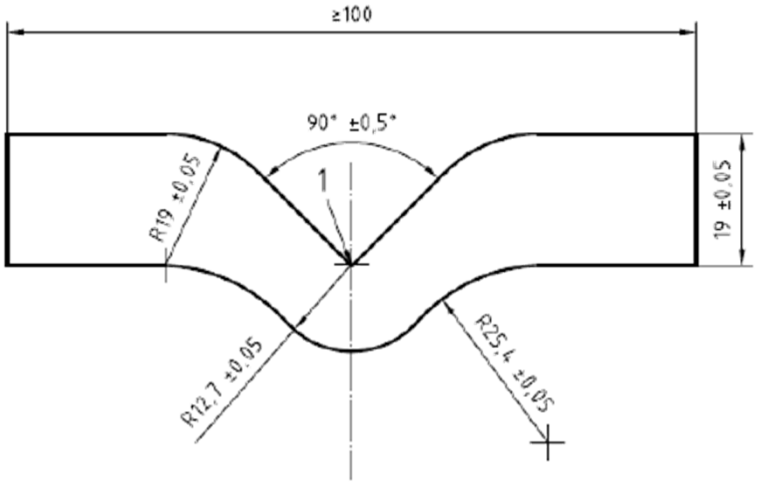
- **Mechanical properties**

STRESS - STRAIN



ISO 37-2:2005

TEAR STRENGTH



ISO 34-1:2004

EXPERIMENTAL TECHNIQUES

- **Hydrolysis resistance: ASTM D471**

Soaking specimens of polyurethanes in water (70ºC during 500 hours)

METHODOLOGY

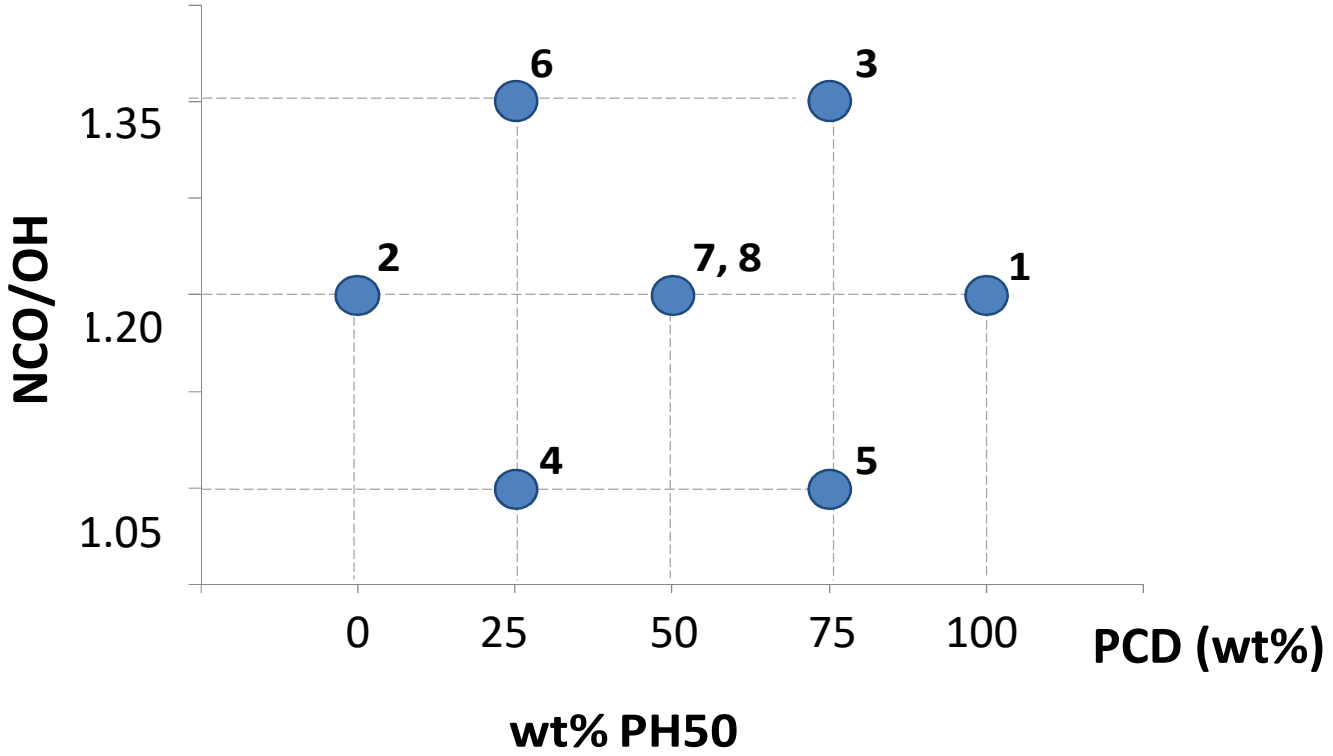
- **Use of experimental design approach (study different variables simultaneously)**

- **Variables to study:**

  - ✓ *Weight content of PCD in polyol mixture (polyether + PCD)*
  - ✓ *NCO/OH ratio*

METHODOLOGY

Doehlert plan



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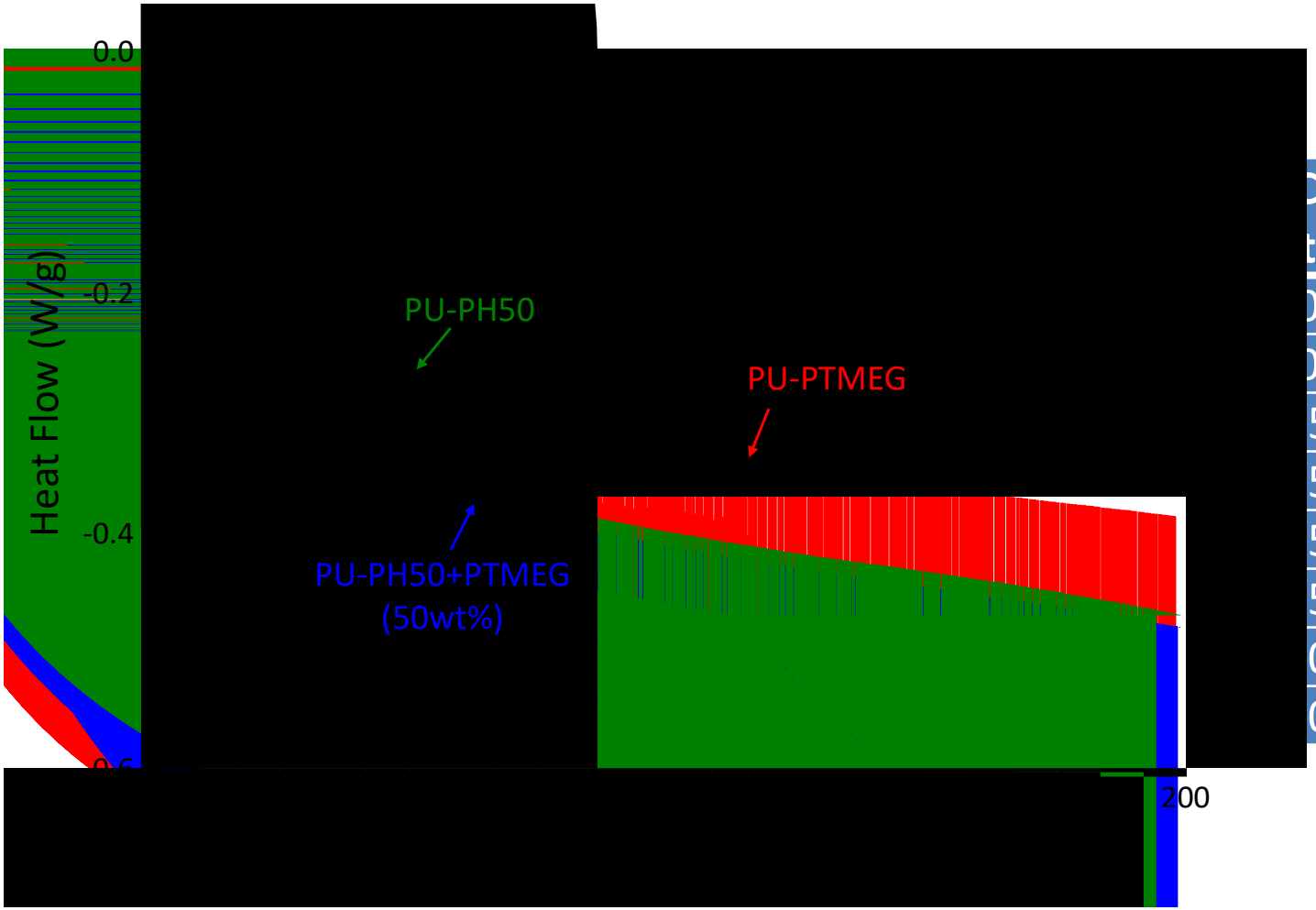
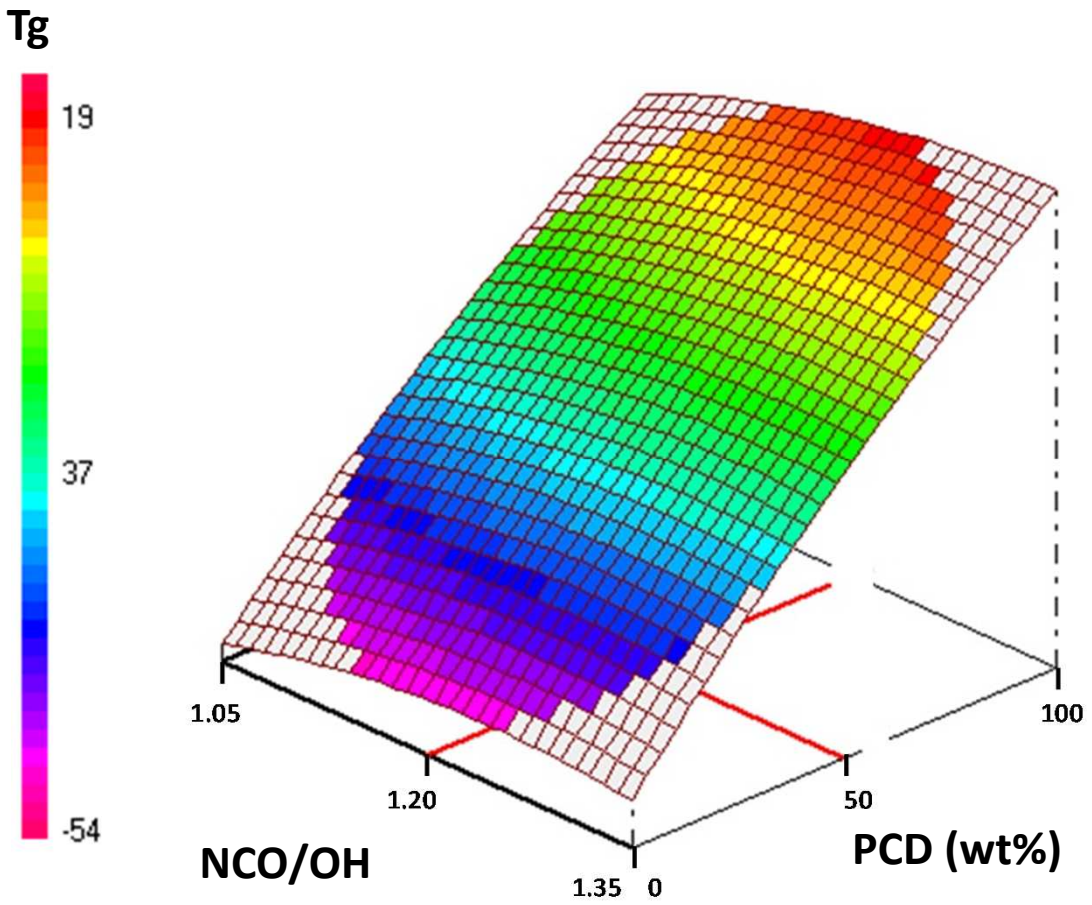
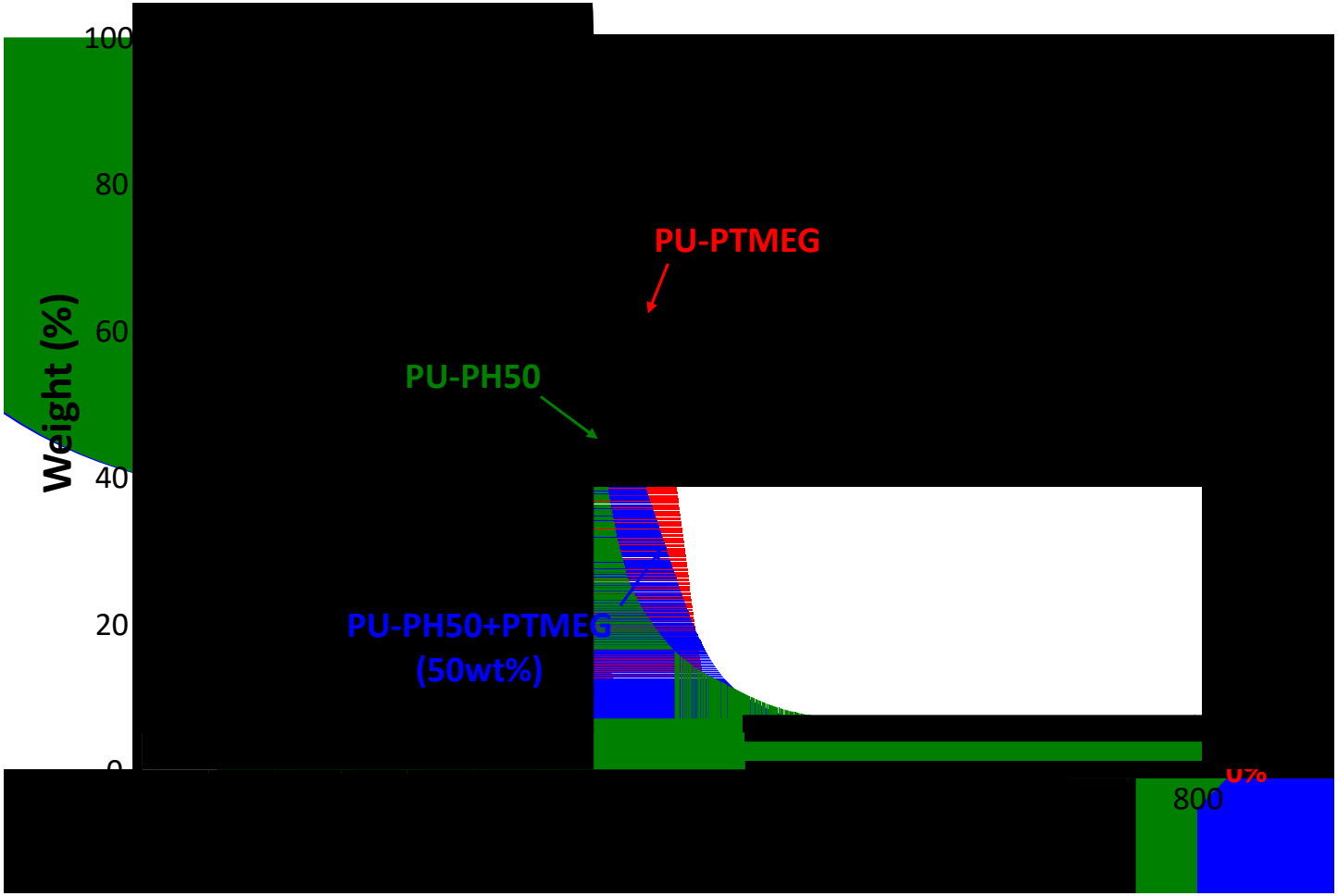
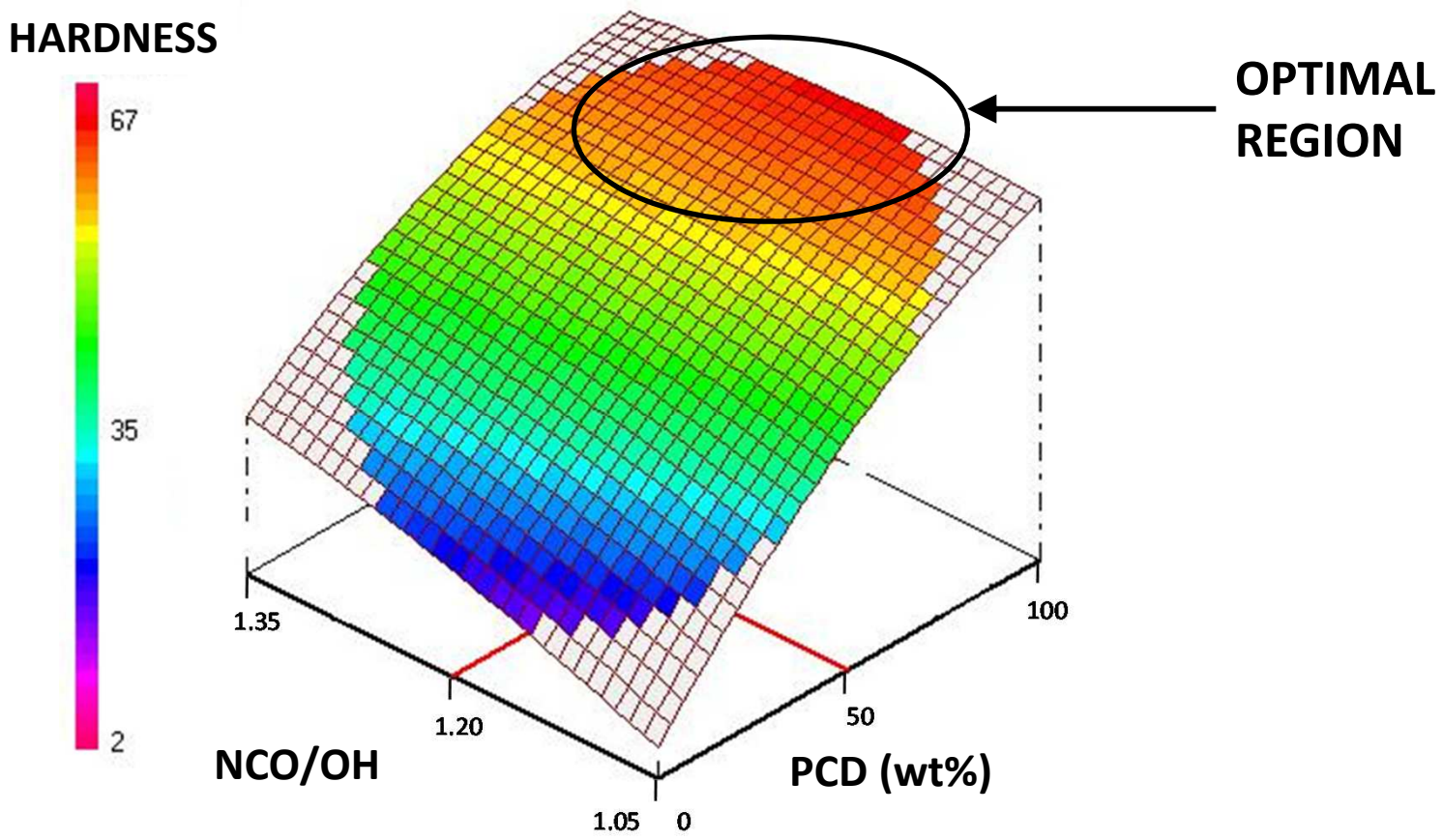


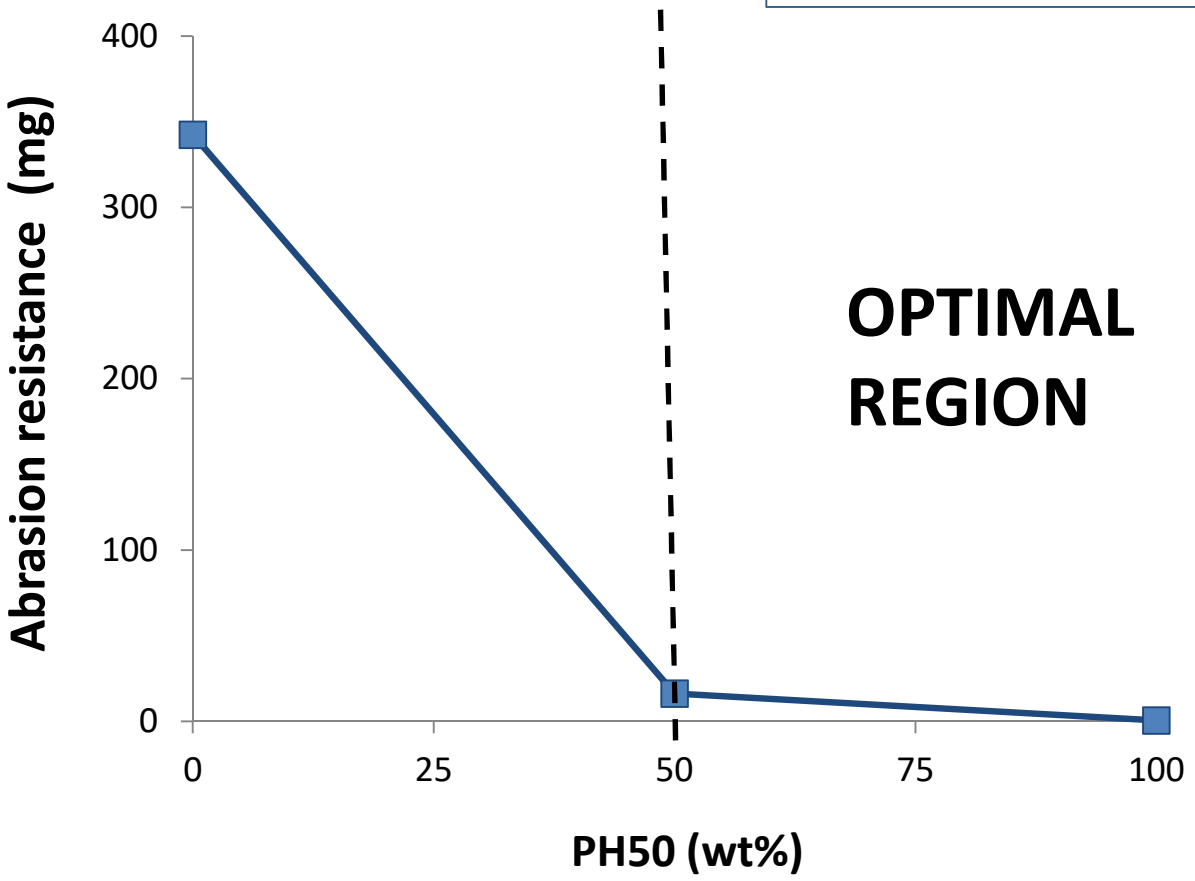
CD t%	NCO/ OH	T_g (ºC)
00	1.20	13
0	1.20	-48
5	1.35	4
5	1.05	-37
5	1.05	-6
5	1.35	-31
0	1.20	-17
0	1.20	-17


Tg
19
37
-54
1.05
1.20
1.35
NCO/OH
0
50
100
PCD (wt%)


100
80
60
40
20
0
Weight (%)
PU-PTMEG
PU-PH50
PU-PH50+PTMEG
(50wt%)
800
U%

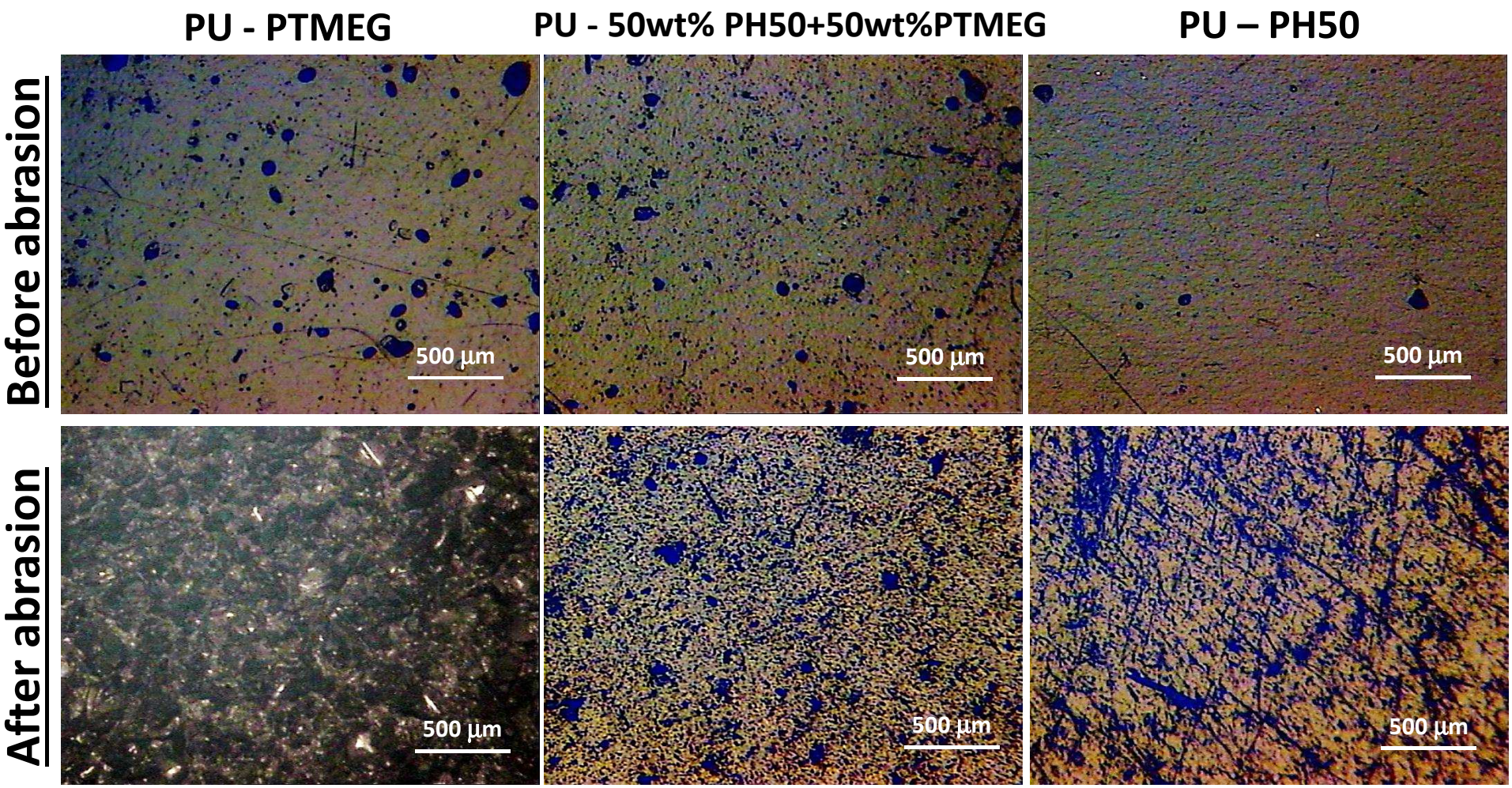

HARDNESS
67
35
2
OPTIMAL
REGION
1.35
1.20
1.05
NCO/OH
0
50
100
PCD (wt%)

PH50 > 50wt%



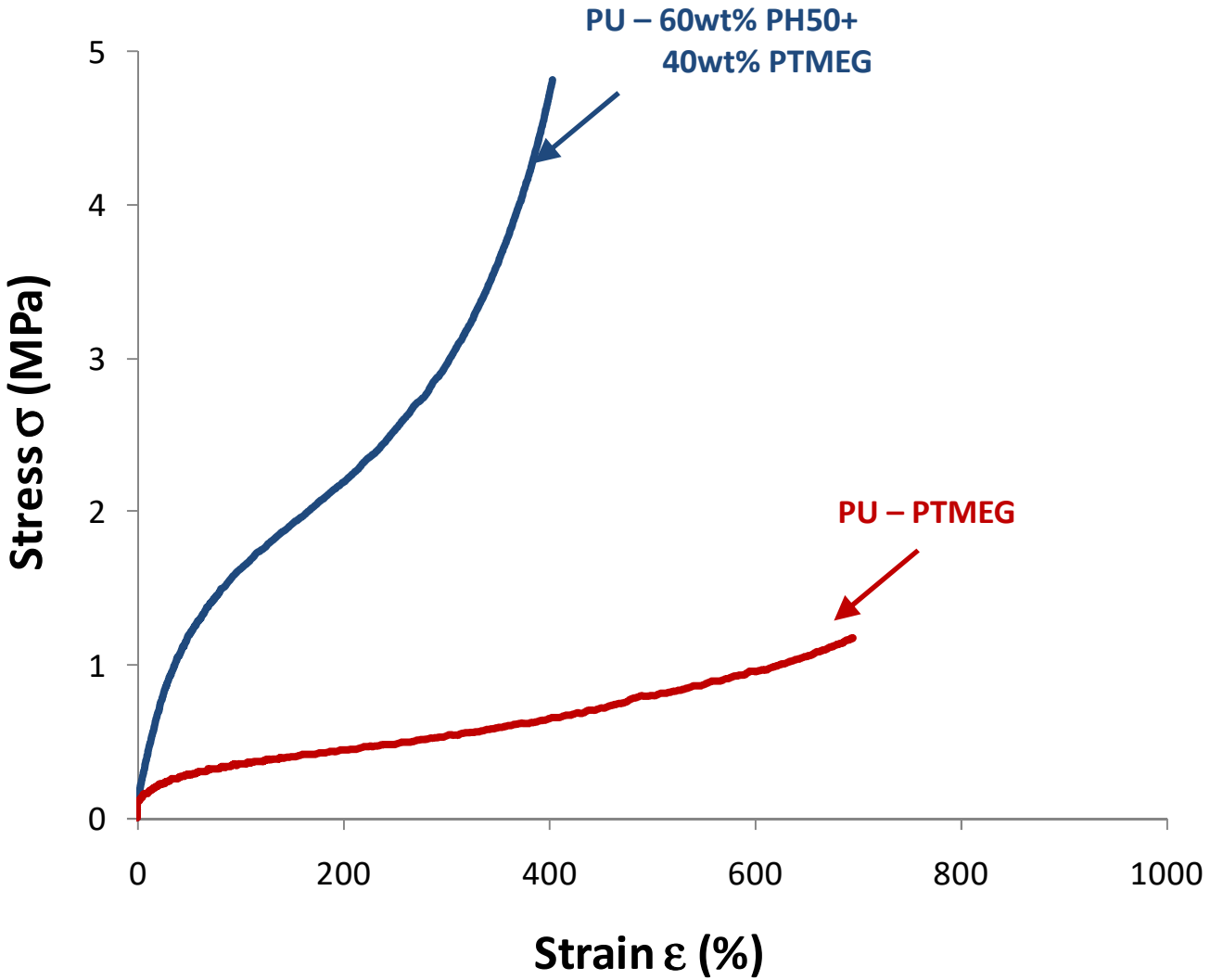
OPTIMAL REGION

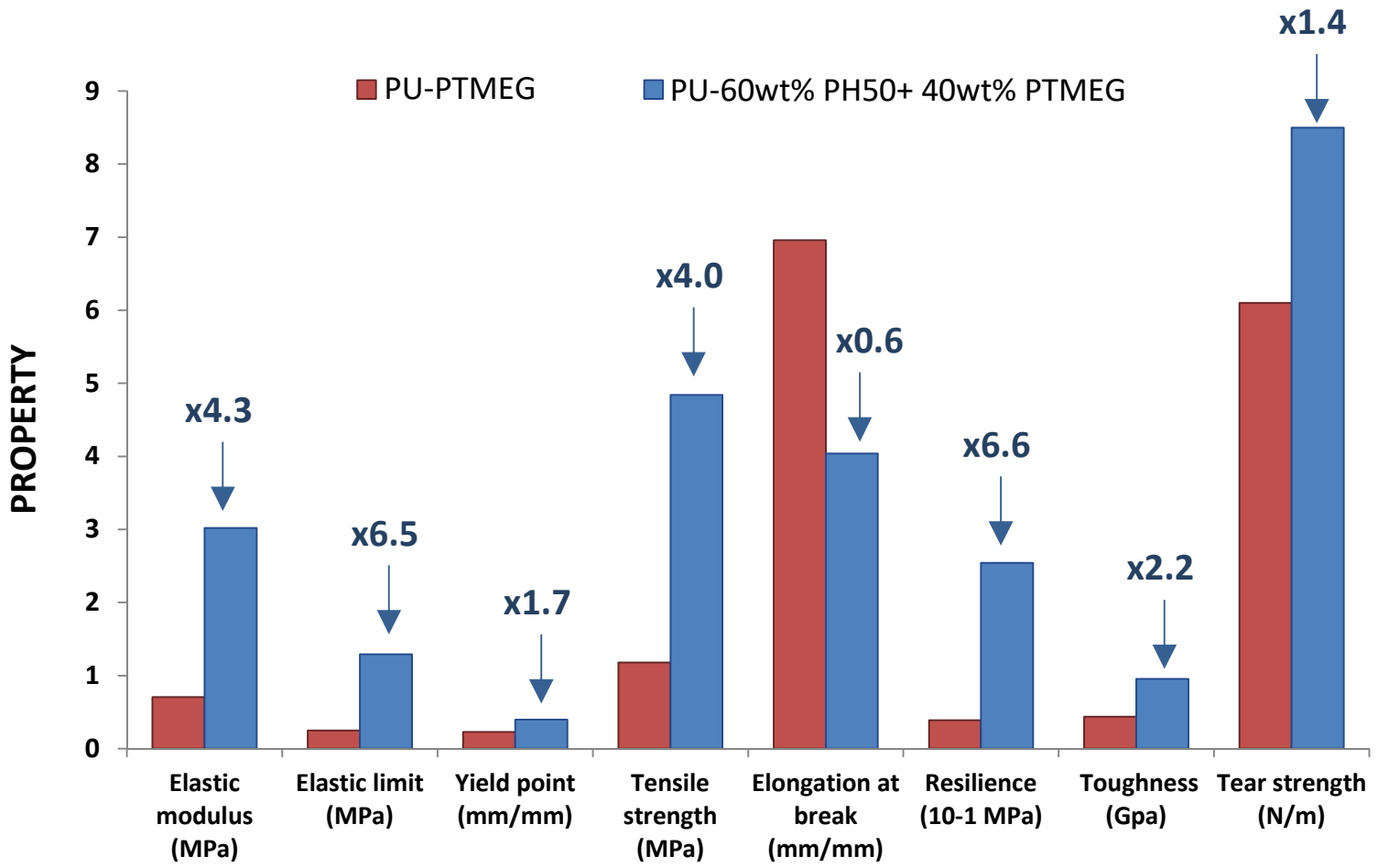
UBE

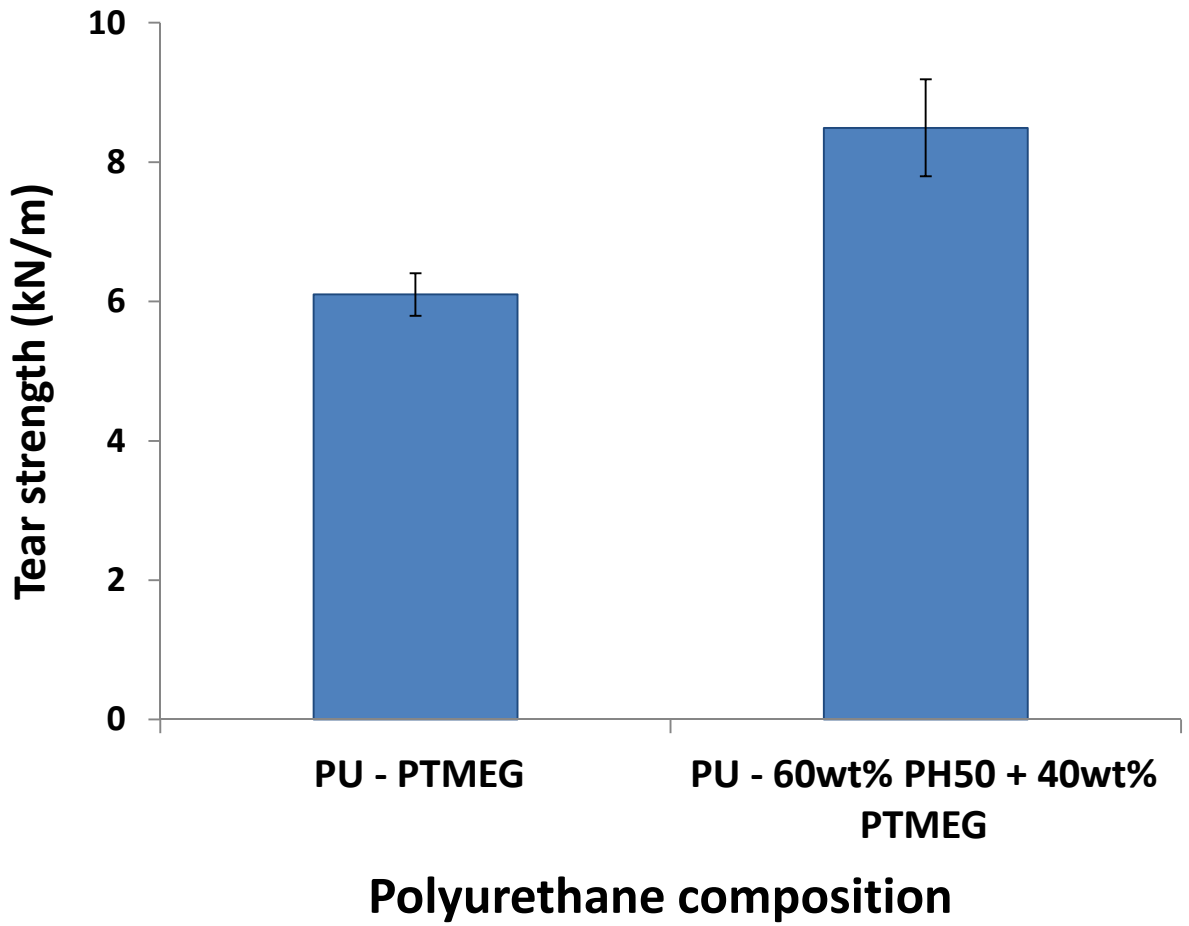


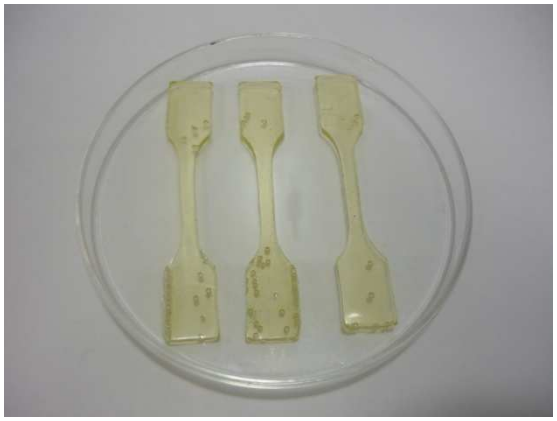
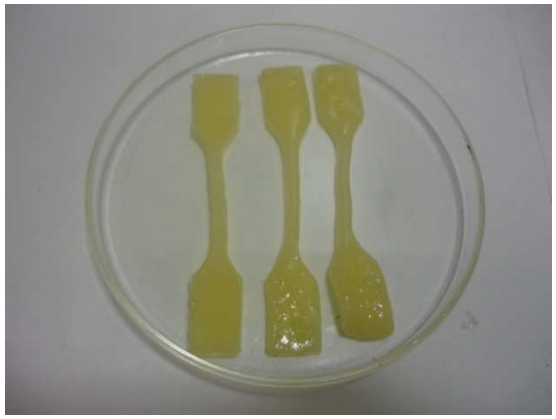
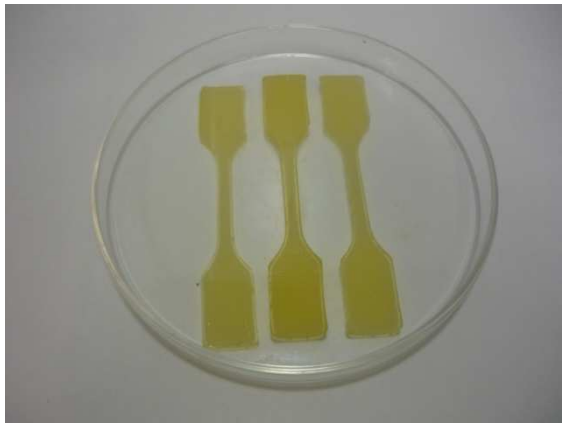
Responsible Care CSR COMPANY

Change & Challenge 2018

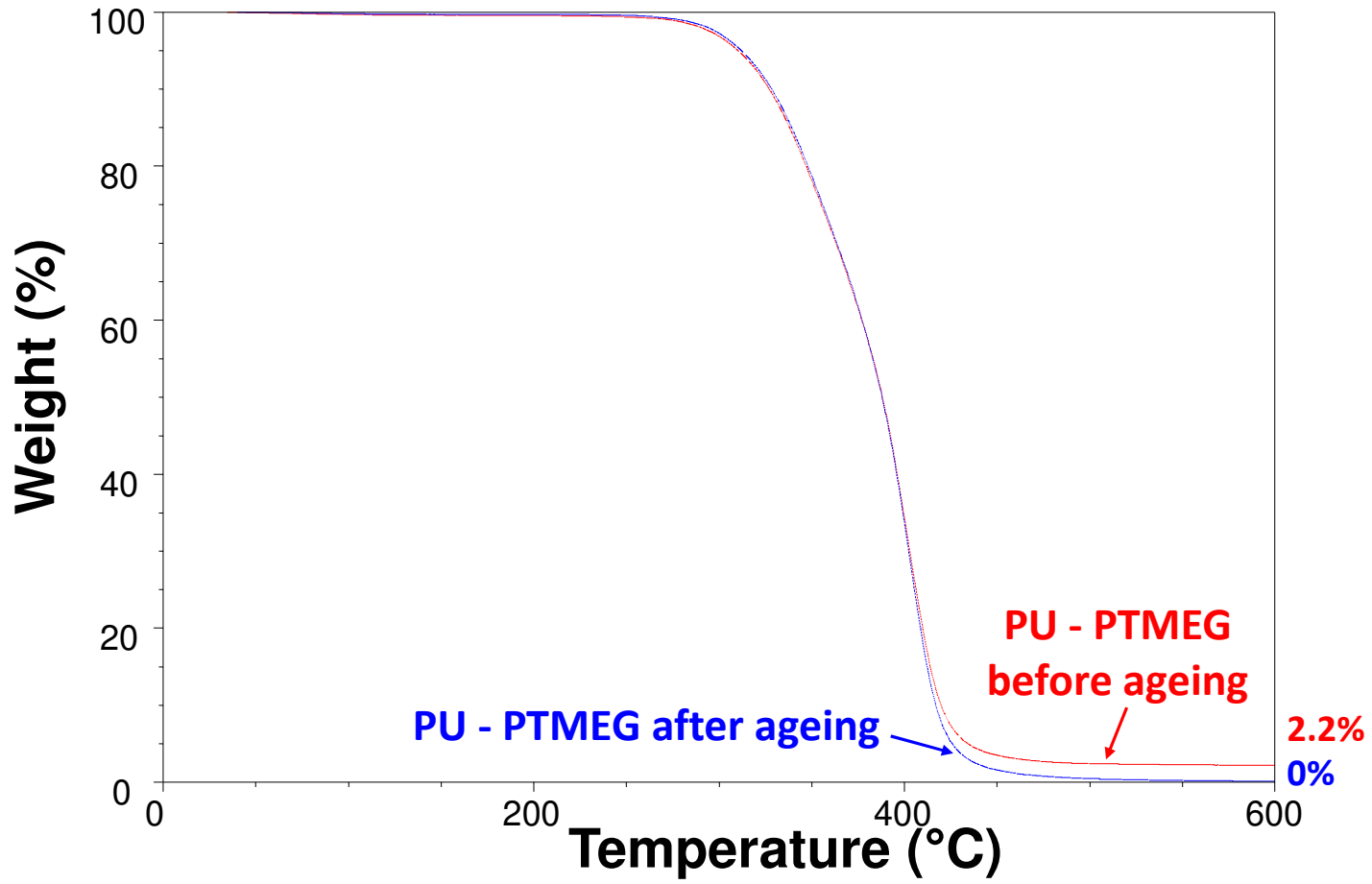

PU – 60wt% PH50+
40wt% PTMEG
PU – PTMEG
Stress σ (MPa)
Strain ε (%)
0
1
2
3
4
5
0
200
400
600
800
1000


PU-PTMEG
PU-60wt% PH50+ 40wt% PTMEG
PROPERTY
0
1
2
3
4
5
6
7
8
9
x4.3
x6.5
x1.7
x4.0
x0.6
x6.6
x2.2
x1.4
Elastic modulus (MPa)
Elastic limit (MPa)
Yield point (mm/mm)
Tensile strength (MPa)
Elongation at break (mm/mm)
Resilience (10-1 MPa)
Toughness (Gpa)
Tear strength (N/m)

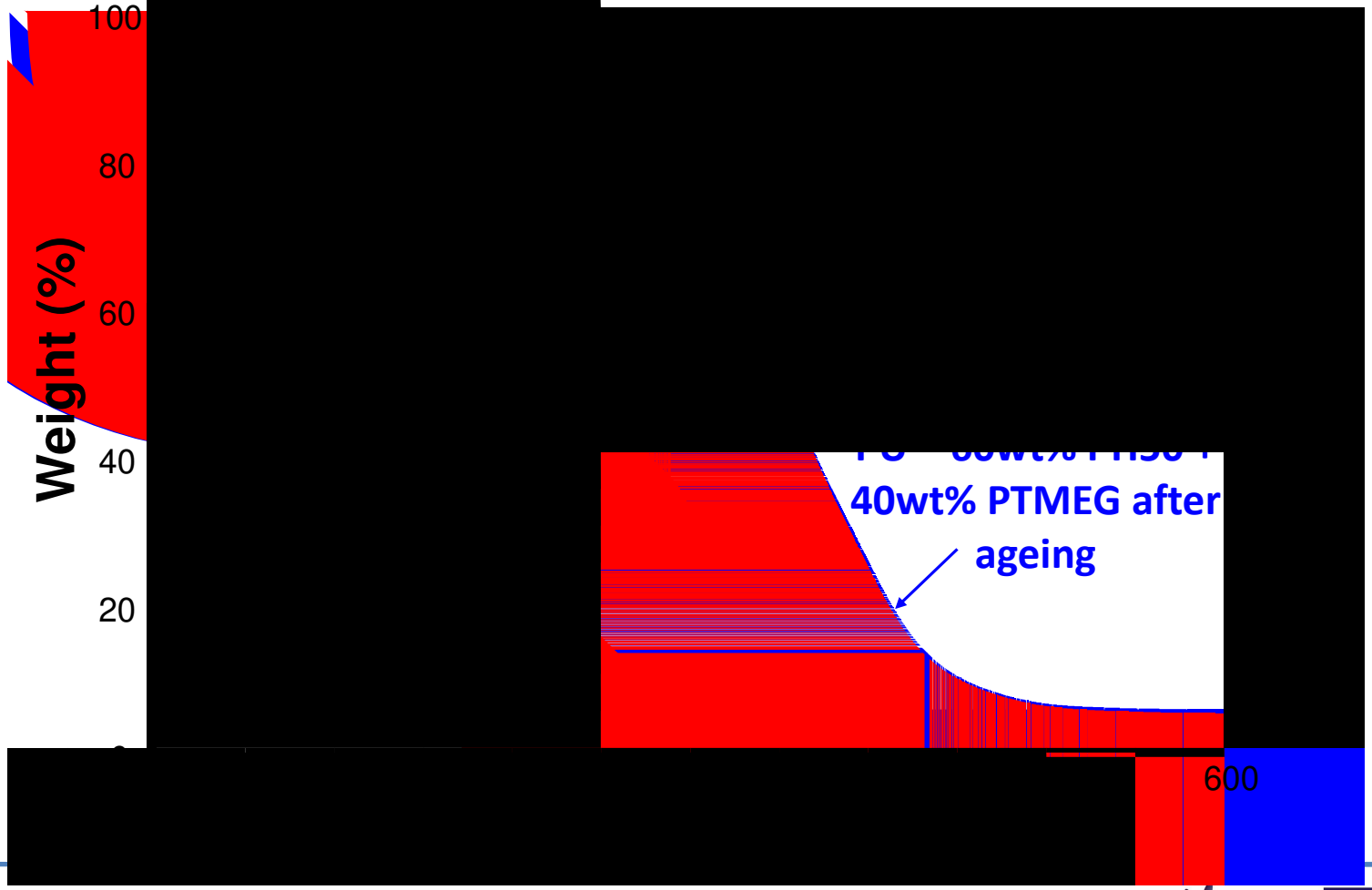

10
8
6
4
2
0
Tear strength (kN/m)
PU - PTMEG
PU - 60wt% PH50 + 40wt% PTMEG
Polyurethane composition

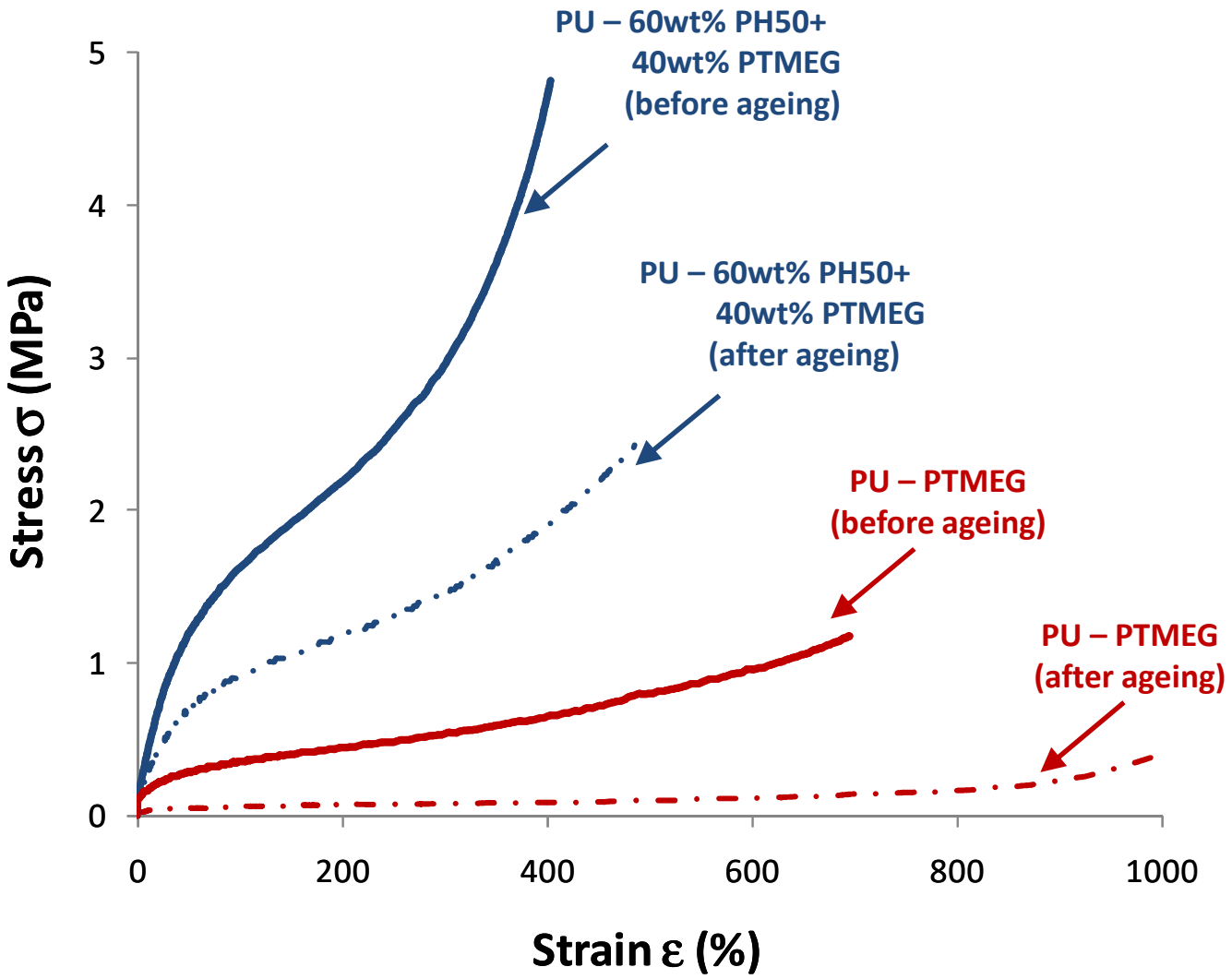
	PU - PTMEG	PU - 60 wt% PH50 + 40 wt% PTMEG
Before ageing		
After ageing		

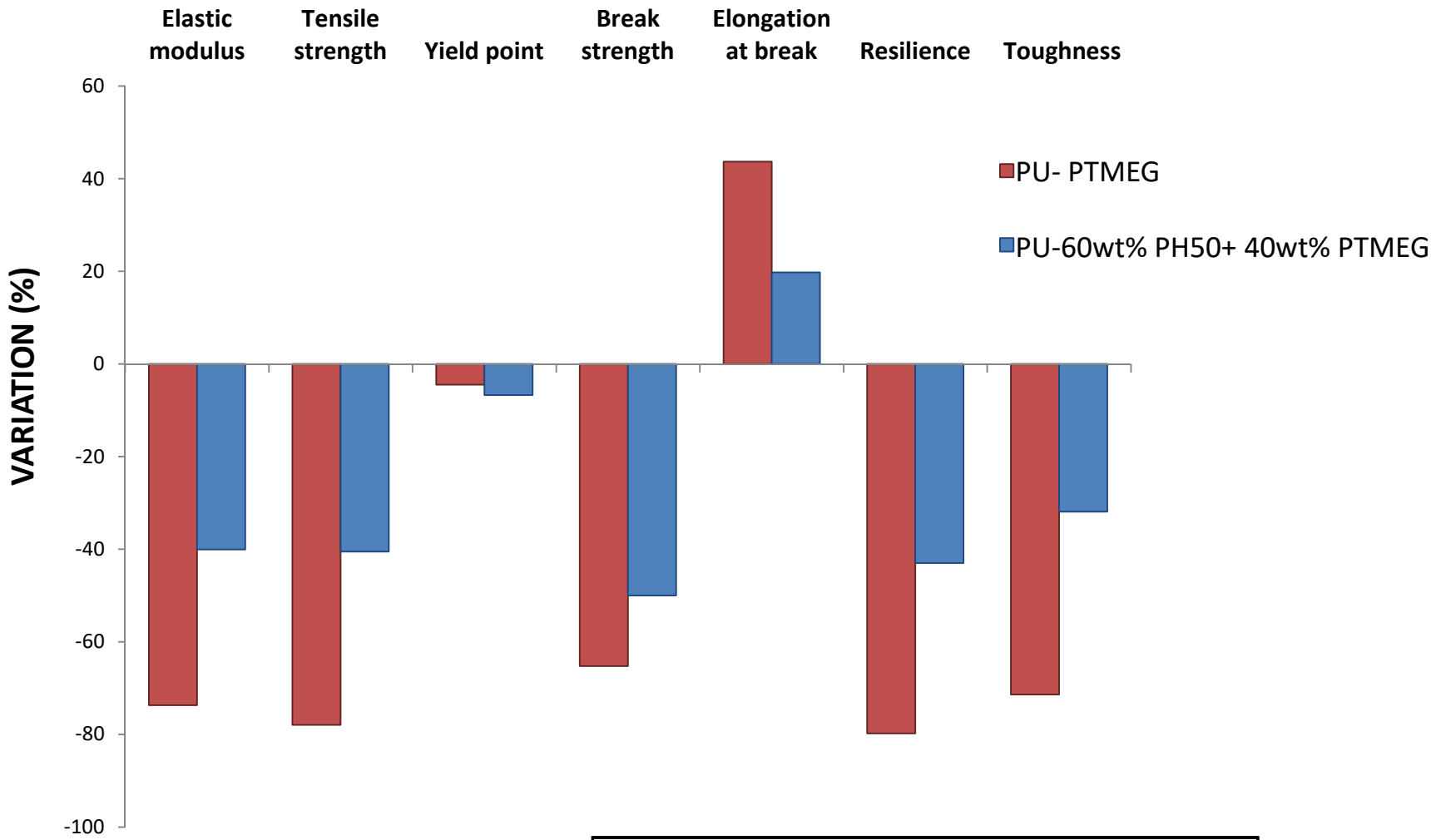
- **PU - PTMEG**


100
80
60
40
20
0
Weight (%)
0
200
400
600
Temperature (°C)
PU - PTMEG
before ageing
PU - PTMEG after ageing
2.2%
0%

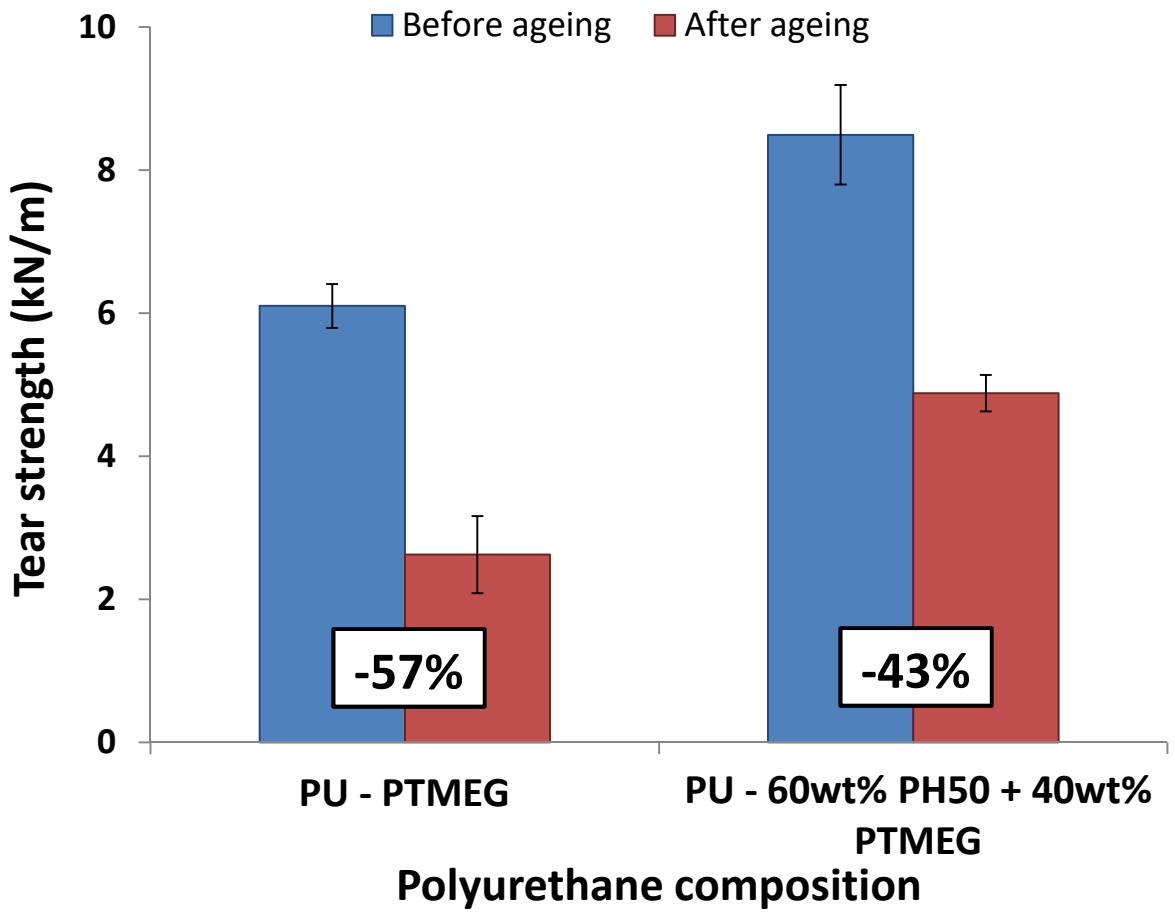
- PU – 60wt%




PU – 60wt% PH50+
40wt% PTMEG
(before ageing)
PU – 60wt% PH50+
40wt% PTMEG
(after ageing)
PU – PTMEG
(before ageing)
PU – PTMEG
(after ageing)
Stress σ (MPa)
Strain ε (%)
0
1
2
3
4
5
0
200
400
600
800
1000



$$\%\ VARIATION = \frac{P_{final} - P_{initial}}{P_{initial}} \times 100$$


Before ageing
After ageing
Tear strength (kN/m)
10
8
6
4
2
0
-57%
-43%
PU - PTMEG
PU - 60wt% PH50 + 40wt% PTMEG
Polyurethane composition

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- Addition of polycarbonate diol → Huge improvement in the mechanical properties of PUs
- PU coating losses by abrasion can be minimized by using polycarbonate diol content higher than 50 wt% in the polyol
- PU coatings with polycarbonate diol showed higher hydrolytic stability and lesser losses of properties after hydrolylic degradation

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***