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

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Change & Challenge
Driving Growth

- Introduction
- Experimental
- Results and discussion
- Conclusions

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- Experimental
- Results and discussion
- Conclusions

- Internal polyurethane coatings of pipelines for improving abrasion resistance

- Current coating : Polyether-based polyurethane

➡ **Polyurethane coatings improved the wear resistance of pipelines under erosion conditions.**

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)

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RESPONSIBLE CARE

UBE

- **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's as pipeline coatings

✓ Limited hydrolytic stability and chemical resistance

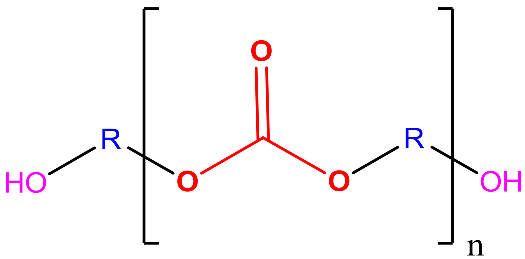
✓ Additives for abrasion improvement are expensive

✓ High costs of maintenance

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

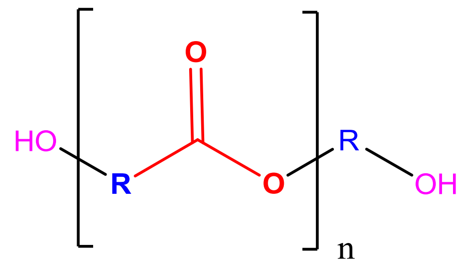
V. García-Pacios, M. Colera, Y. Iwata, J.M. Martín-Martínez. ***«Incidence of the polyol nature in waterborne polyurethane dispersions on their performance as coatings as stainless steel»*** Progress in Organic Coatings 276 (12), 1726-1729 (2013)

Terminal – Backbone – Bridge – Backbone – Terminal



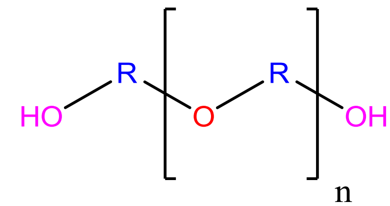
Polycarbonate diol

higher stability due to lower chemical reactivity



Polyester diol

poor hydrolysis resistance



Polyether diol

low radical oxidation stability

<u>Advantages of polycarbonate diol</u>: Carbonate vs. ester & ether as bridge

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


Automotive


Artificial leather


Leather finishing


Automotive finishing


Flooring


Wood coating & paints


Adhesives


Bioadhesives


TPU & elastomers


Rollers


Footwear


RIM foams

Any other application requesting improved durability…

➡ Advantages of polycarbonate diols for pipelines:

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

Challenge
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➡ **Objectives**

- Improve the mechanical properties and abrasion resistance
- Improve the durability

of internal PU coatings for pipelines by using polycarbonate diol in their synthesis

- Introduction
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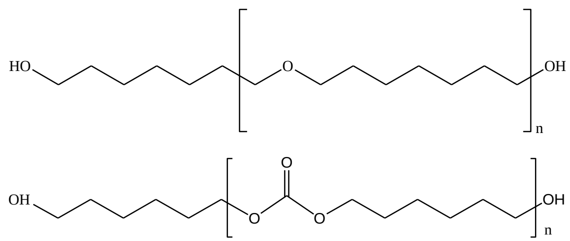
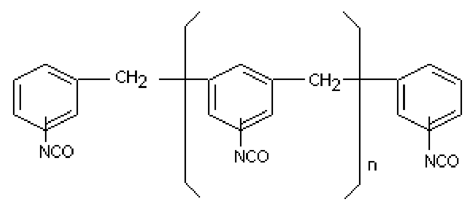
UBE

SYNTHESIS OF PU's

- **Polyurethane coatings obtained by «one shot» process:**



Polyether diol + polycarbonate diol



Polymeric MDI

1,4-butanediol

↓

Polyurethane

RAW MATERIALS

➡ **Polyols**

- Polyether: Polytetramethyleneglycol (PTMG)
- Polycarbonate diol: ETERNACOLL® PH50

PTMG
Sigma Aldrich Ltd.
(St. Paul, MN, USA)
M_w = 1000 Da

Eternacoll® PH50
UBE Chemical Europe S.A.
(Castellón, Spain)
M_w = 500 Da

RAW MATERIALS

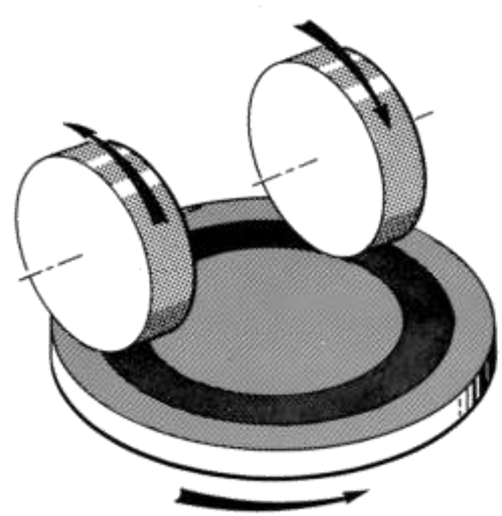
- **Isocyanate: Polymeric MDI (pMDI)**
- **Chain extender: 1,4-butanediol**

SUPRASEC® 2416
Huntsman International LLC
(Woodlands, TX, USA)

1,4-butanediol
Sigma Aldrich Ltd.
(St. Paul, MN, USA)

EXPERIMENTAL TECHNIQUES

- **Wear resistance: ASTM D4060**



Rotational abrameter Taber 5135
Taber Industries
(North Tonawanda, NY, USA)

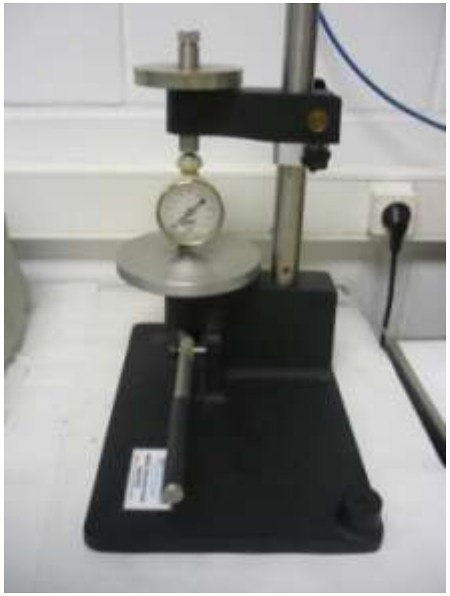
EXPERIMENTAL TECHNIQUES

- Optical microscopy

Laborlux 12 ME ST
Leica Microsystems GmbH
(Wetzlar, Germany)

EXPERIMENTAL TECHNIQUES

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



Durotech BS550 – Pin Load Instron (ASTM D2240)
Hampden Test Equipment Ltd.
(Northampton, UK)

EXPERIMENTAL TECHNIQUES

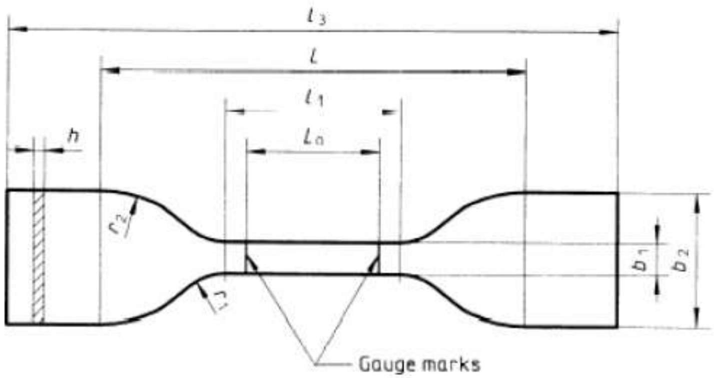
➡ Mechanical properties

Universal Testing Machine Instron 4411
Instron Corp.
(Norwood, MA, USA)

EXPERIMENTAL TECHNIQUES

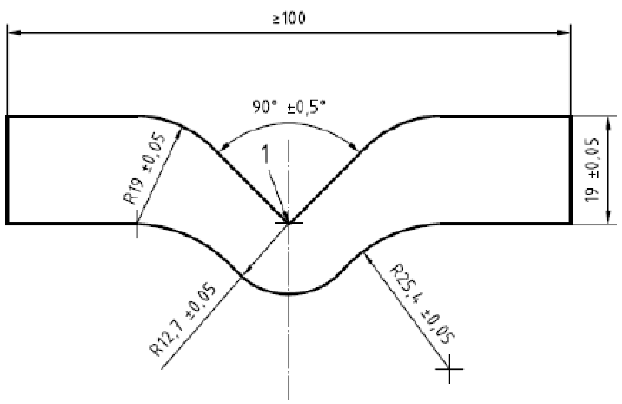
➡ **Mechanical properties**

STRESS - STRAIN



ISO 37-2:2005

TEAR STRENGTH



ISO 34-1:2004

EXPERIMENTAL TECHNIQUES

- **Hydrolysis resistance: ASTM D471**

Soaking specimens of polyurethanes in water at 70ºC for 500 hours

METHODOLOGY

- **Use of experimental design approach to study different variables simultaneously**

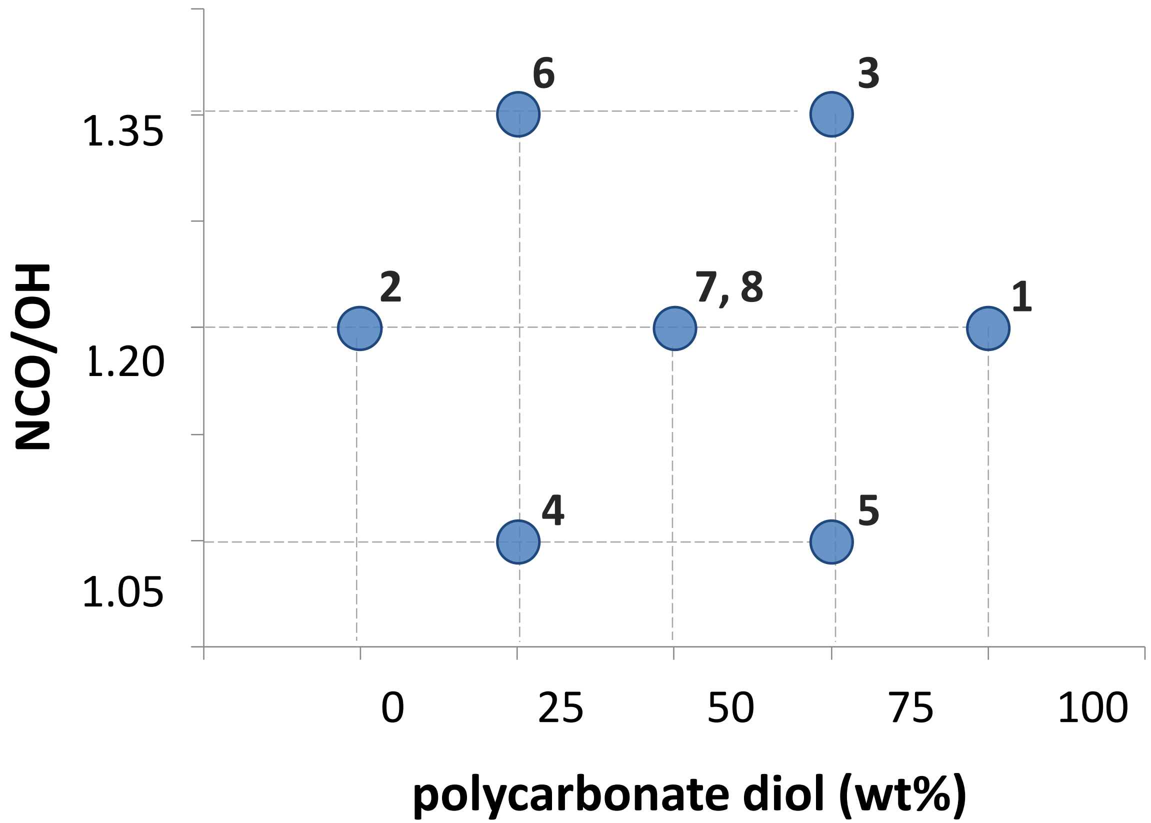
- **Variables to study:**

  ✓ Weight content of polycarbonate diol in the polyol mixture of polyether + polycarbonate diol

  ✓ NCO/OH ratio

METHODOLOGY

Doehlert plan



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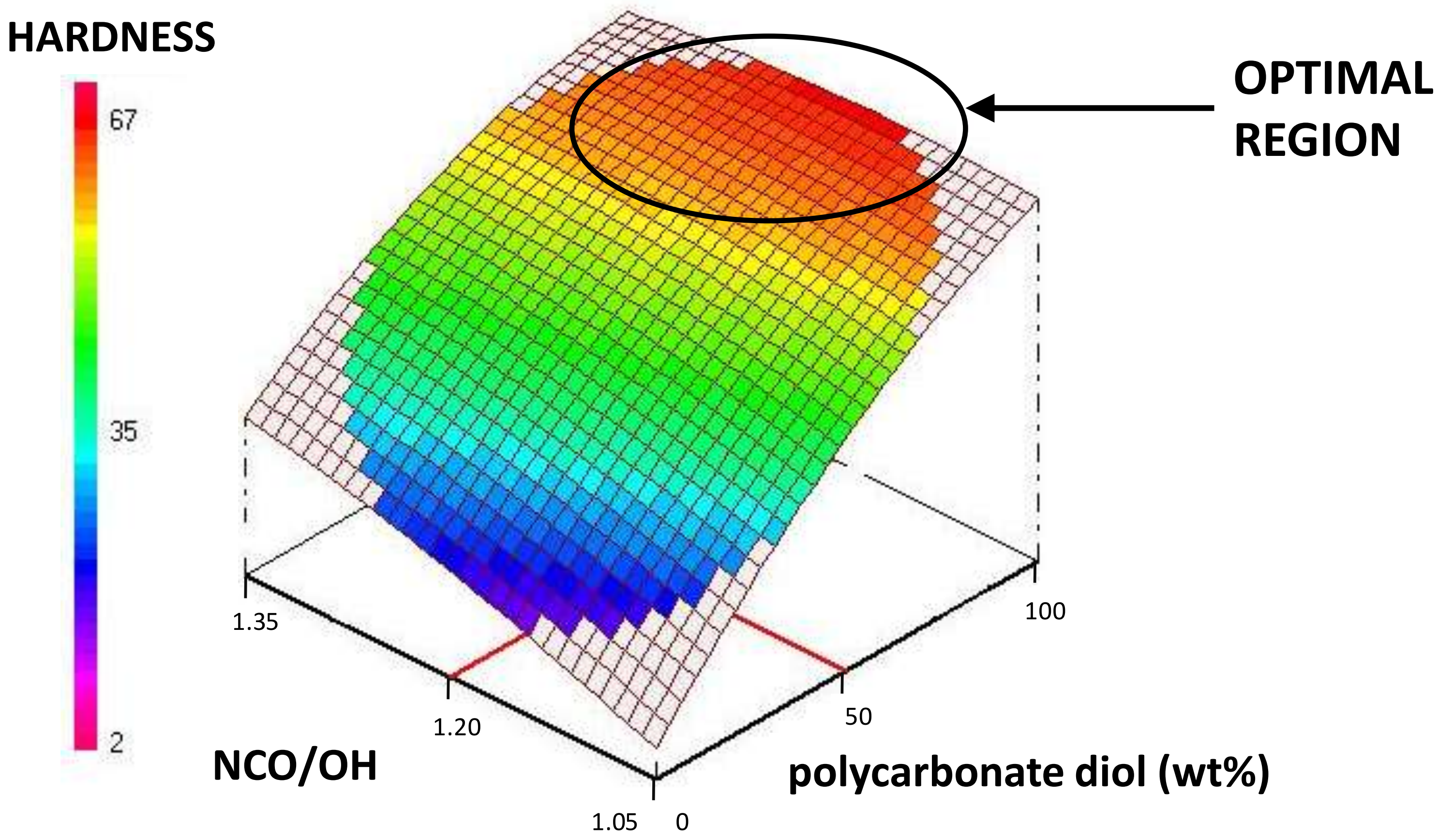
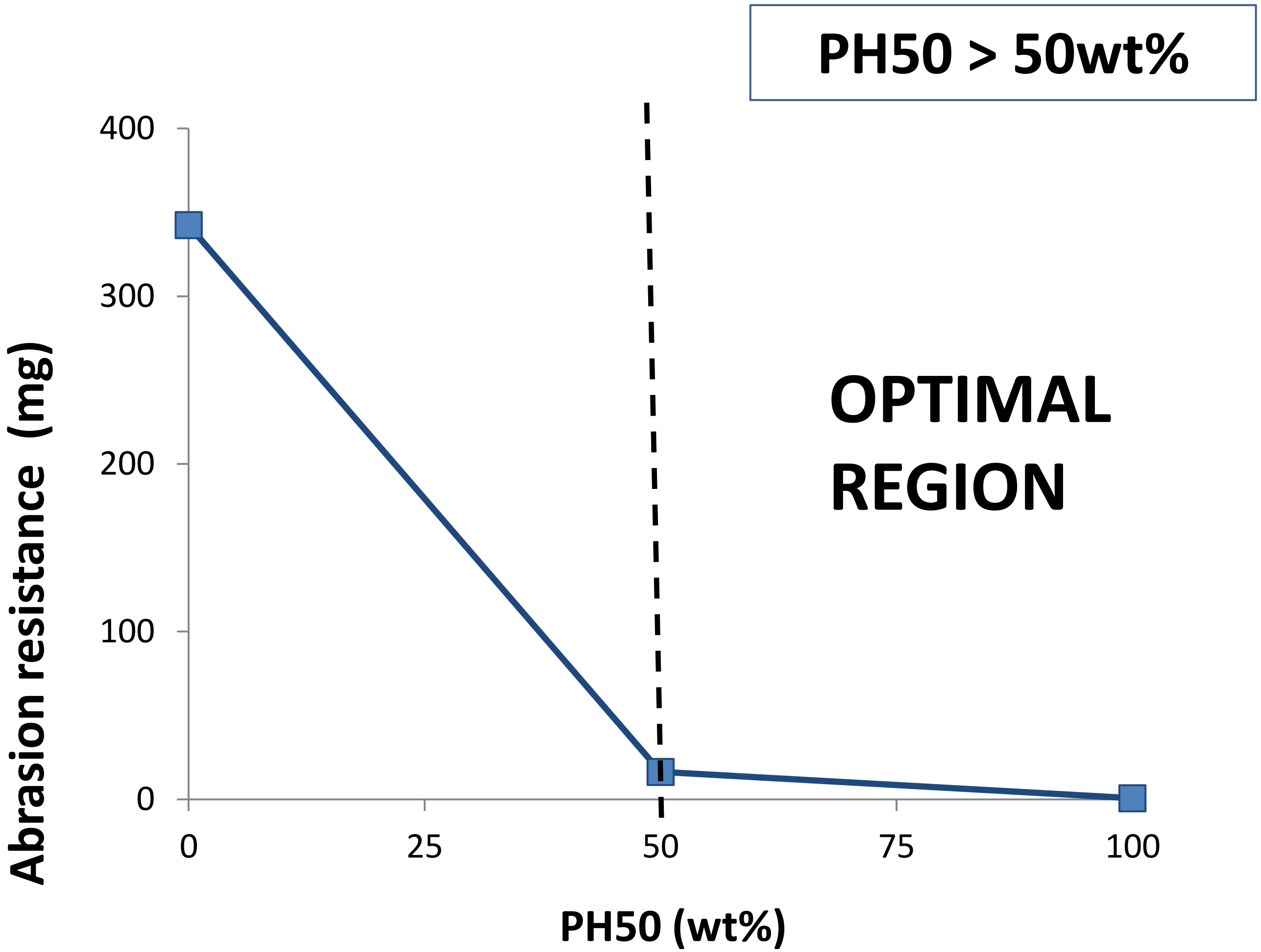
Formulation	Pot life (min)	Viscosity (mPa · s)	Abrasion resistance (mm^3)
Specification	10 -16	< 2000	< 50 mm
Polycarbonate diol-free blank	on spec	on spec	34
PH50-including optimization	13.5	870	4

- **With the optimized formulation containing polycarbonate diol as polyol (polyol blend: PH50 60% - PTMG 40%)**
  a. **Pot life: Pot life of the castable PU mixture is on specification, meeting similar curing times than those polycarbonate diol-free formulations**
  b. **Viscosity: As above, comparable viscosities are reached when including polycarbonate diol as polyol**
  c. **Abrasion resistance: PH50 increases the abrasion resistance of final polyurethane**


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

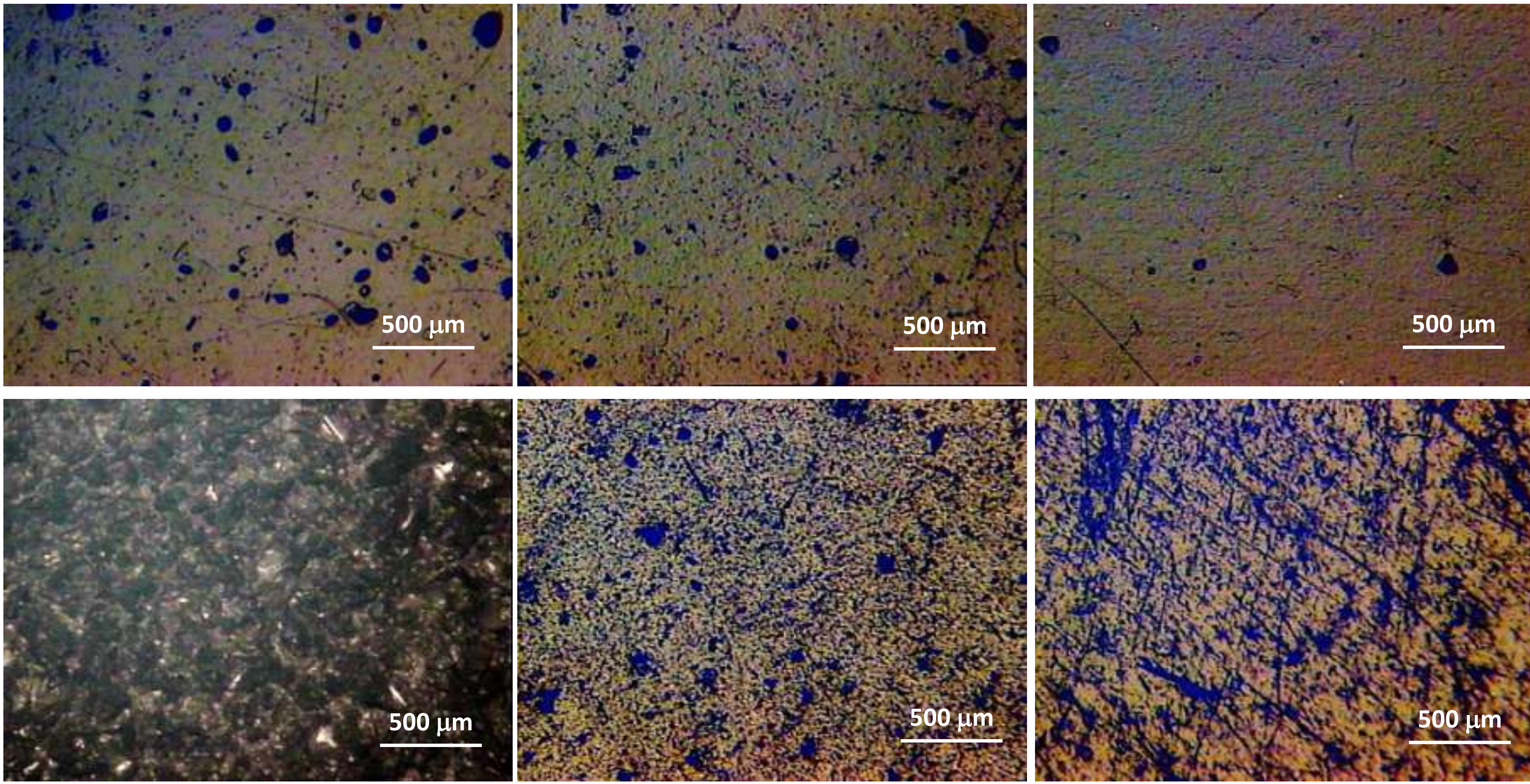


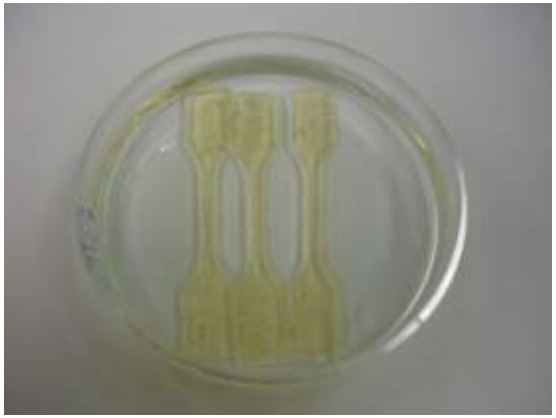
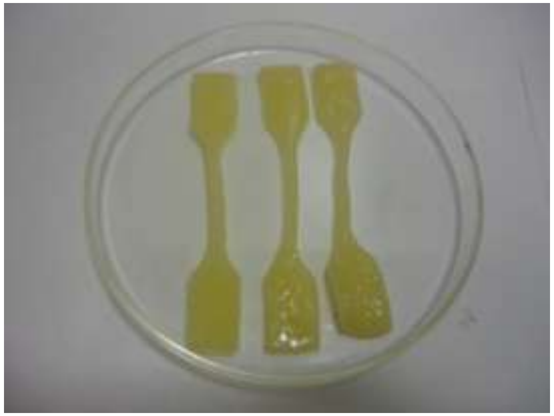
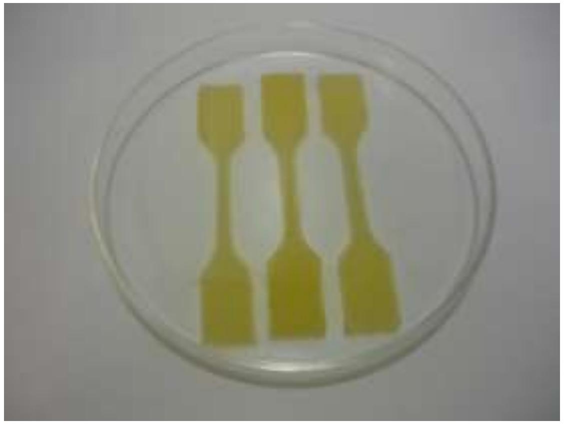
PH50 > 50wt%
OPTIMAL REGION
Abrasion resistance (mg)
400
300
200
100
0
0
25
50
75
100
PH50 (wt%)

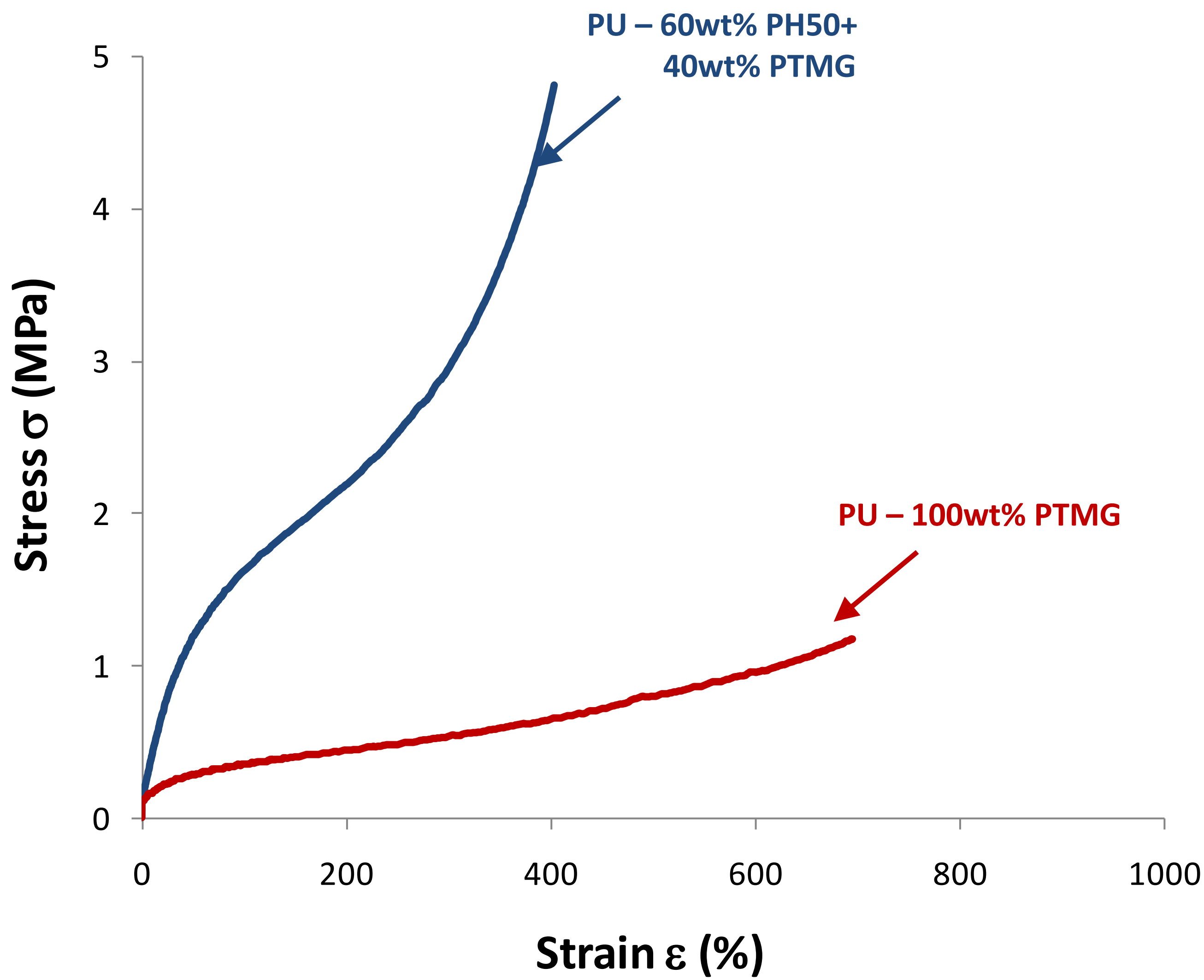
	100wt% PTMG	50wt% PTMG + 50wt% polycarbonate diol	100wt% polycarbonate diol

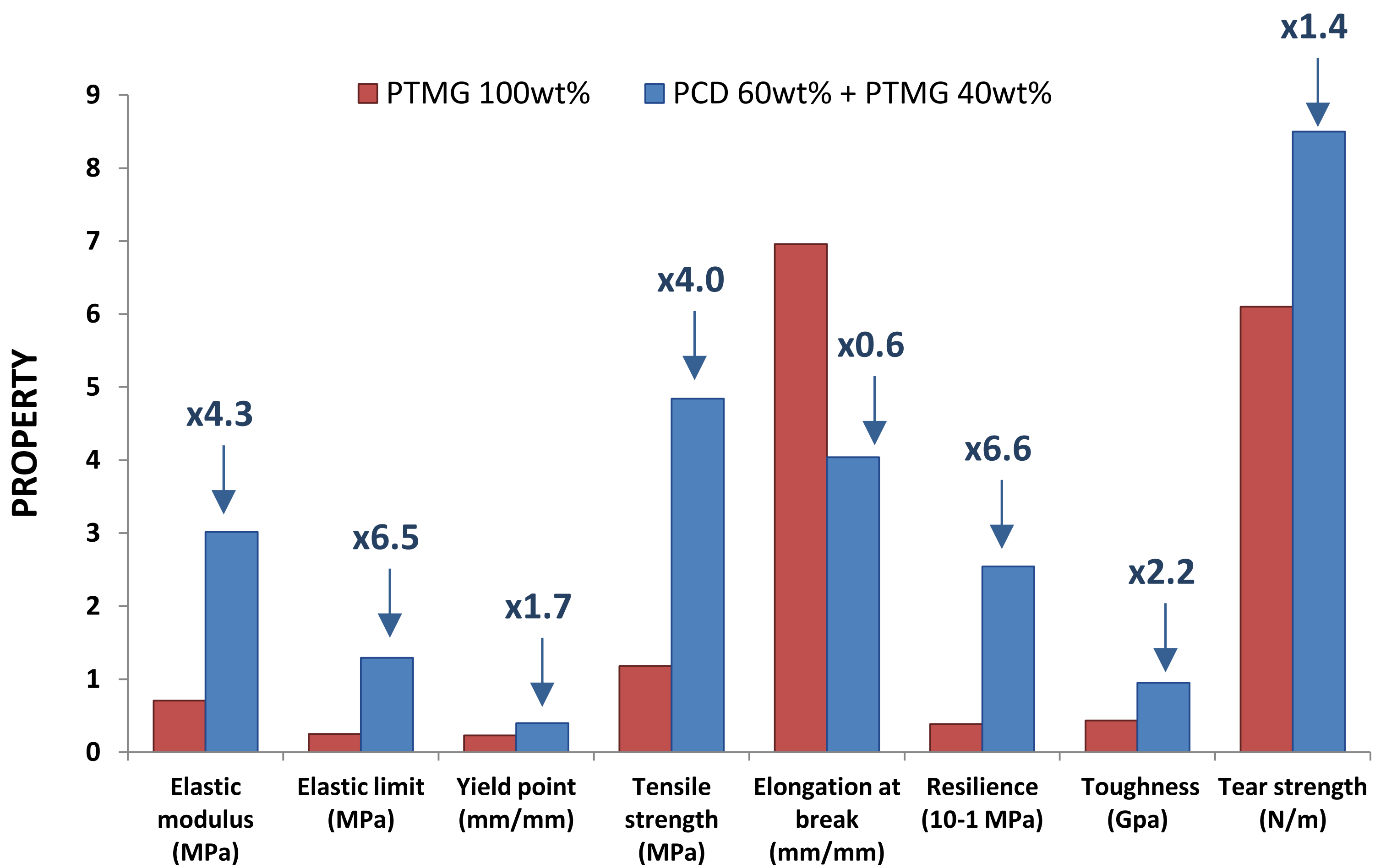
Before abrasion

After abrasion



	100 wt% PTMG	60 wt% PH50 + 40 wt% PTMG
Before ageing		
After ageing		


PU – 60wt% PH50+
40wt% PTMG
PU – 100wt% PTMG
Stress σ (MPa)
0
1
2
3
4
5
0
200
400
600
800
1000
Strain ε (%)



Challenge
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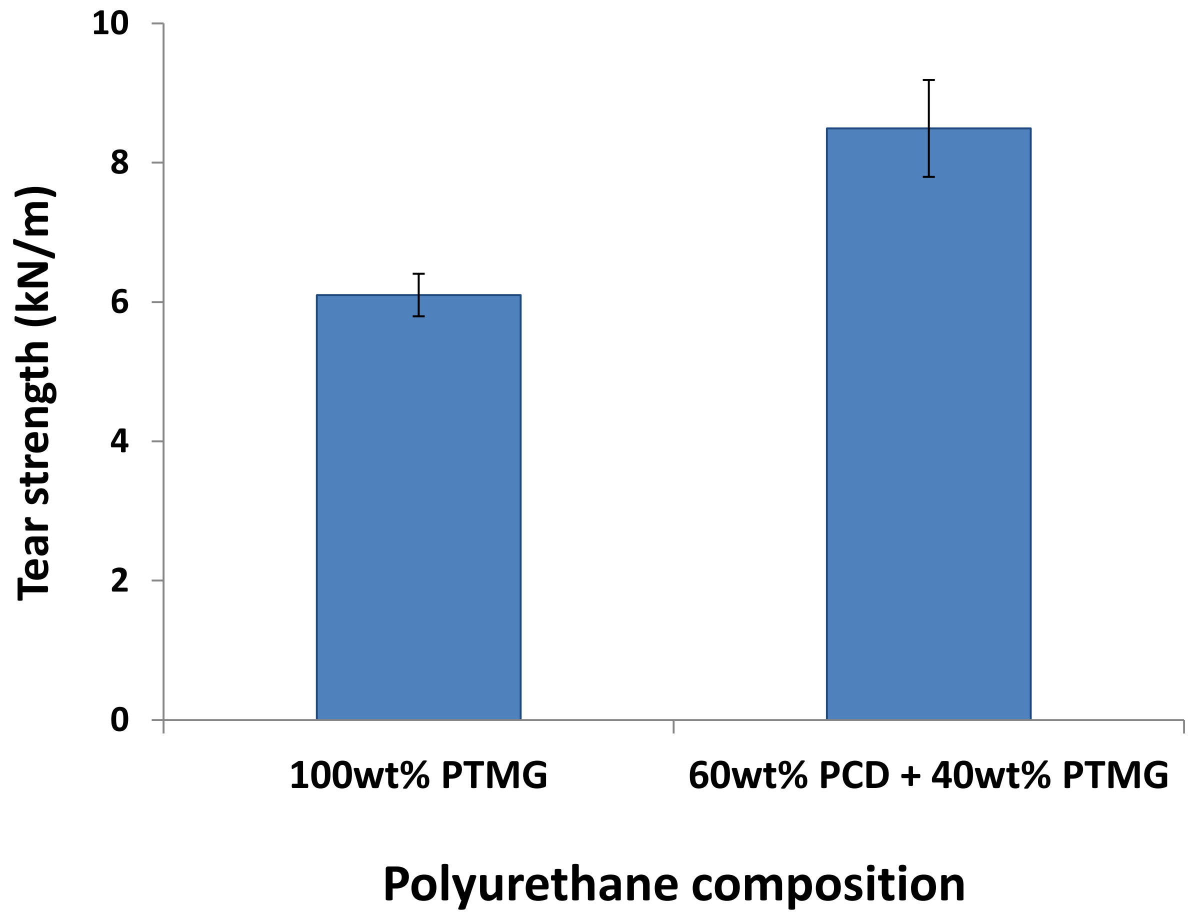
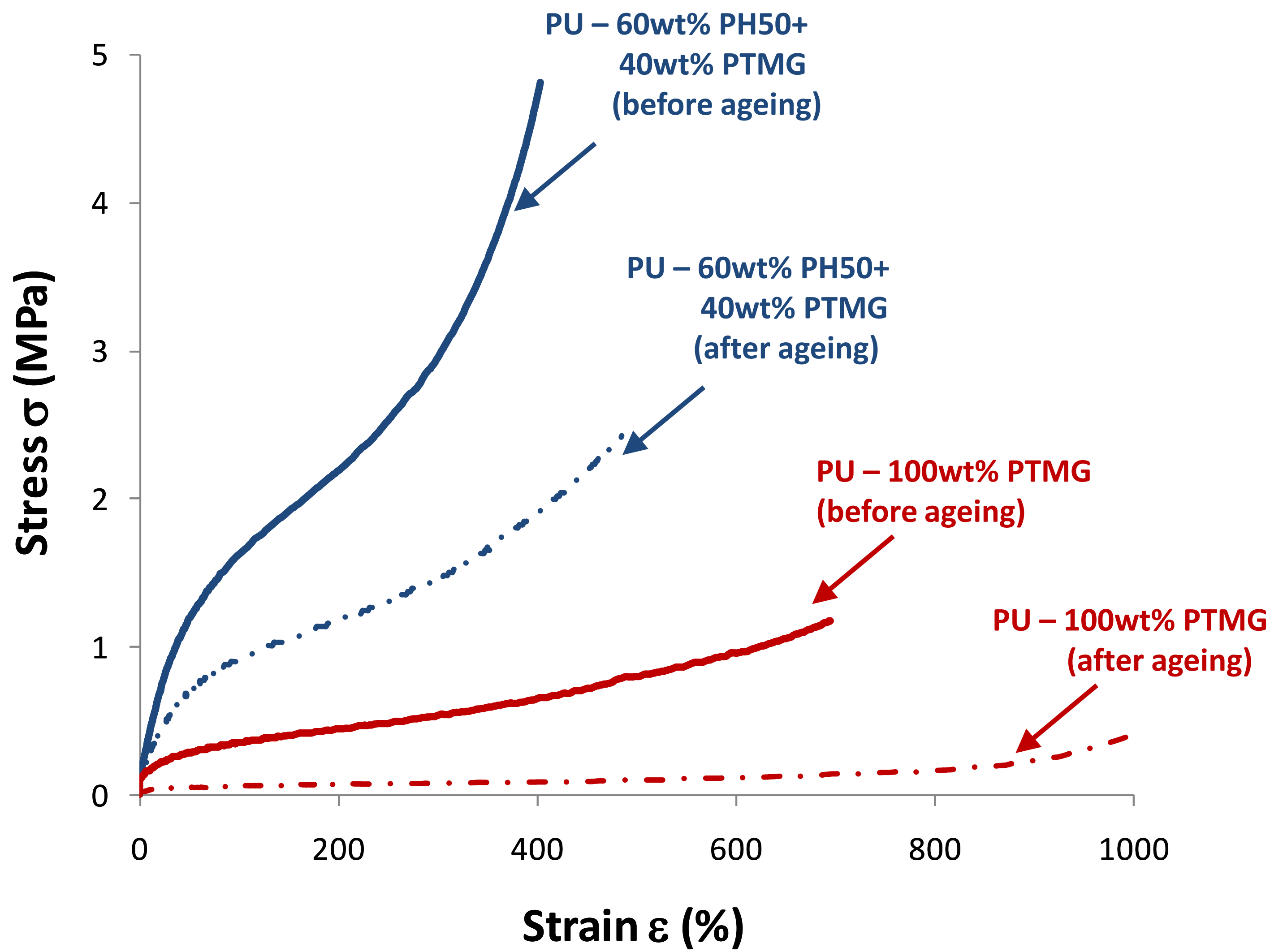
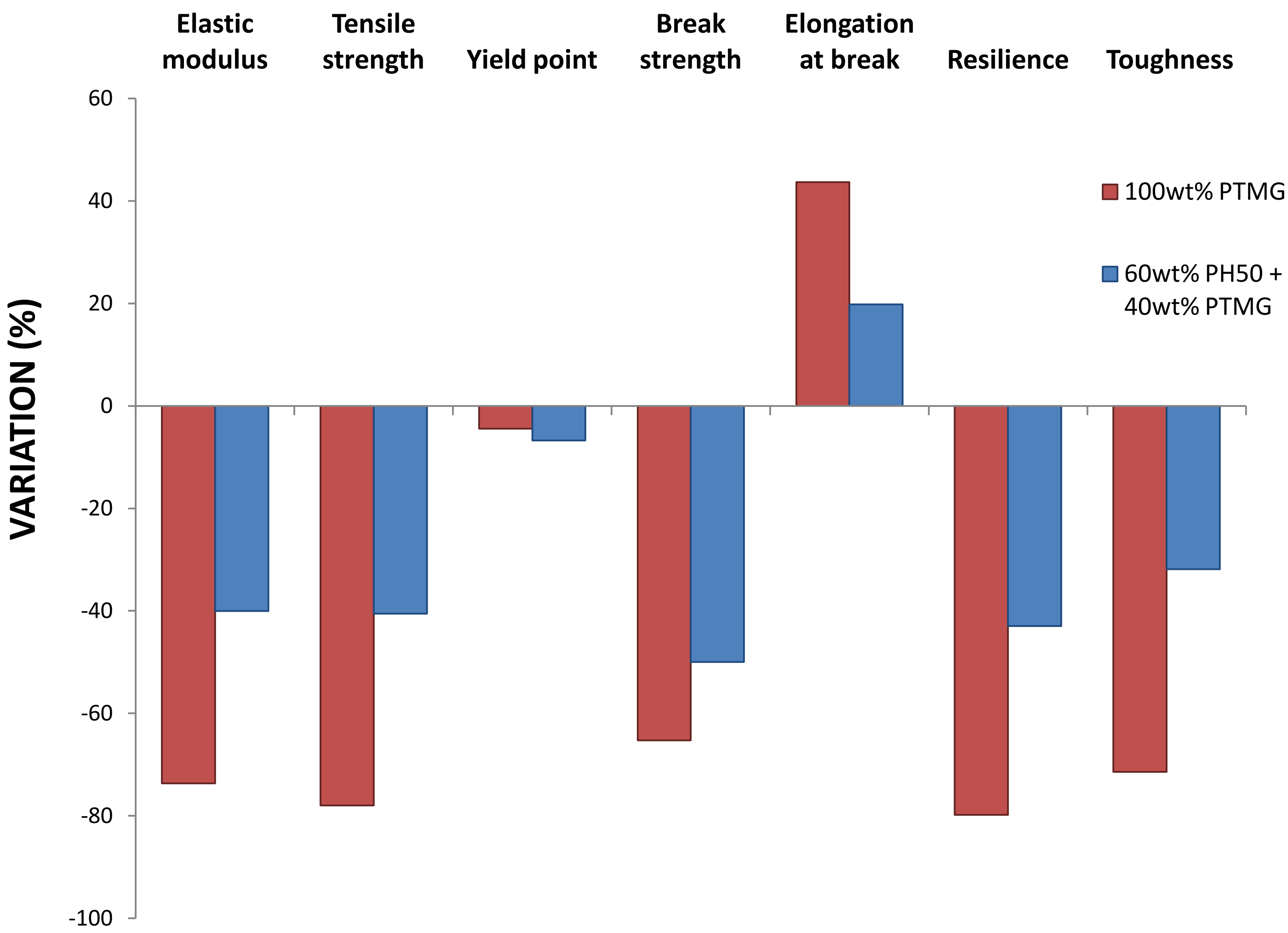
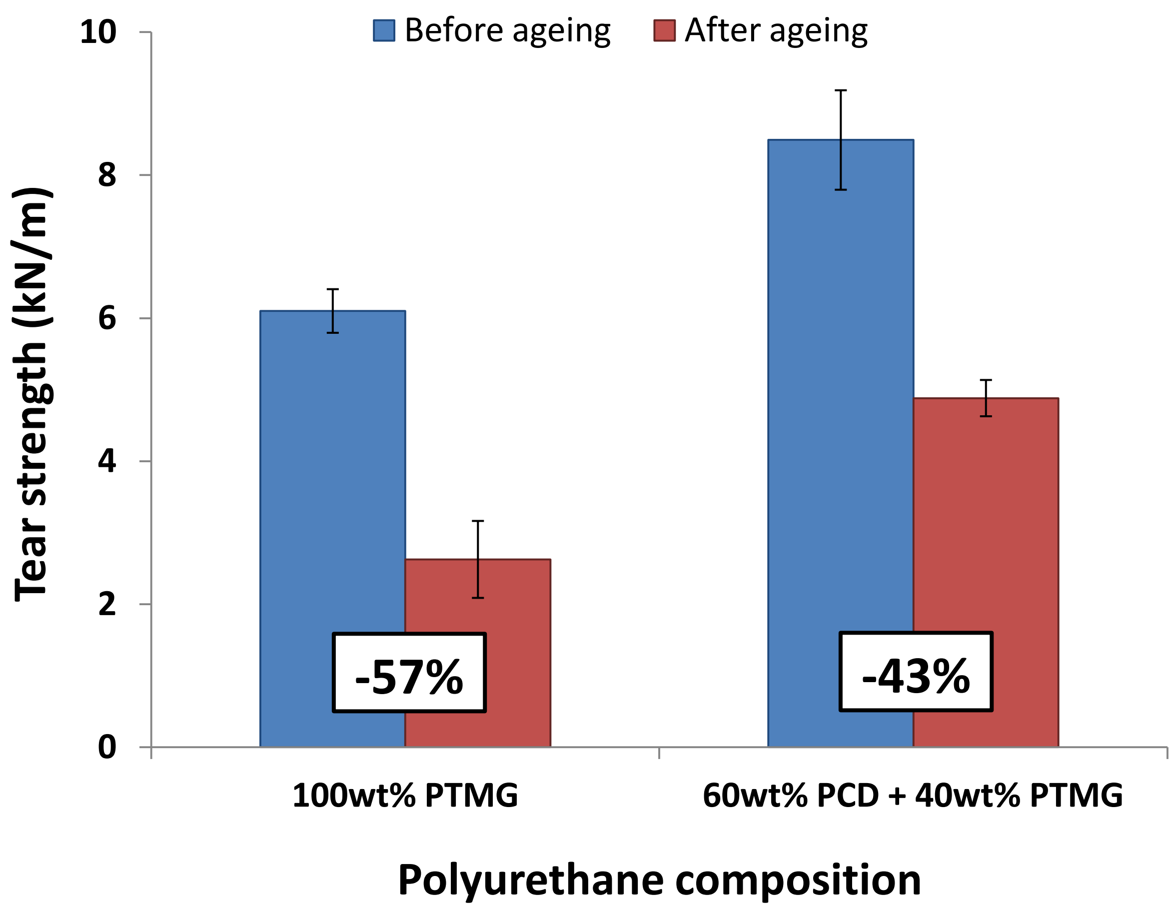
RESPONSIBLE CARE



Tear strength (kN/m)
10
8
6
4
2
0
100wt% PTMG
60wt% PCD + 40wt% PTMG
Polyurethane composition


PU – 60wt% PH50+
40wt% PTMG
(before ageing)
PU – 60wt% PH50+
40wt% PTMG
(after ageing)
PU – 100wt% PTMG
(before ageing)
PU – 100wt% PTMG
(after ageing)
Stress σ (MPa)
Strain ε (%)
0
1
2
3
4
5
0
200
400
600
800
1000


Elastic modulus
Tensile strength
Yield point
Break strength
Elongation at break
Resilience
Toughness
VARIATION (%)
60
40
20
0
-20
-40
-60
-80
-100
100wt% PTMG
60wt% PH50 + 40wt% PTMG



Before ageing
After ageing
10
8
6
4
2
0
Tear strength (kN/m)
-57%
-43%
100wt% PTMG
60wt% PCD + 40wt% PTMG
Polyurethane composition

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- Addition of polycarbonate diol produced a huge improvement in the mechanical properties of polyurethanes
- PU coating losses by abrasion can be minimized by using polycarbonate diol content higher than 50 wt% in the polyol
- PU coatings containing polycarbonate diol showed high hydrolytic stability and less losses of properties after hydrolylic degradation

Muito Obrigado !!!

Deseja melhorar a performance dos Poliuretanos em sua aplicação?
Deseja maiores informações sobre Eternacoll® Polycarbonate diols?

- ✓ ***Visite nossa webpage www.ube.es***
- ✓ ***Envie um e-mail a d.Hernandes@ube.ind.br***
- ✓ ***Fale com Daniel Hernandes – 11 9 6640 6053***