

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

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- ➔ Introduction
- ➔ Experimental
- ➔ Results and discussion
- ➔ Conclusions

- ➔ **Introduction**
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- ➔ 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)

- ➔ **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)

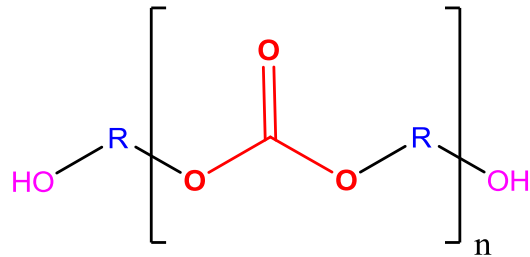
- ➔ **Current drawbacks and limitations of PU's as pipeline coatings**
  - ✓ **Limited hydrolytic stability and chemical resistance**
  - ✓ **Additives for abrasion improvement are expensive**
  - ✓ **High costs of maintenance**

- ➔ 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)

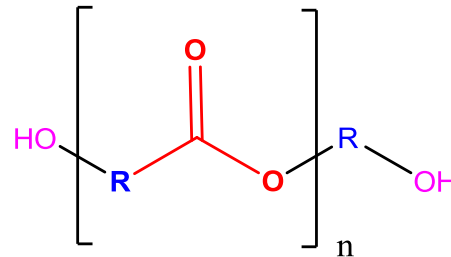


## Terminal – Backbone – Bridge – Backbone – Terminal



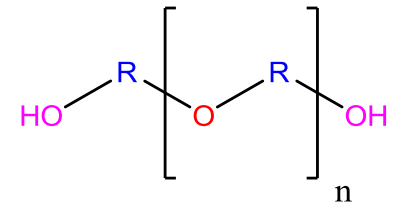
*Polycarbonate diol*

higher stability due to  
lower chemical reactivity



*Polyester diol*

poor hydrolysis resistance



*Polyether diol*

low radical oxidation stability

### Advantages of polycarbonate diol: 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







Oil & mining



Encapsulation



Pavements



Inks



Waterproof membranes

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

## ➔ Objectives

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

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

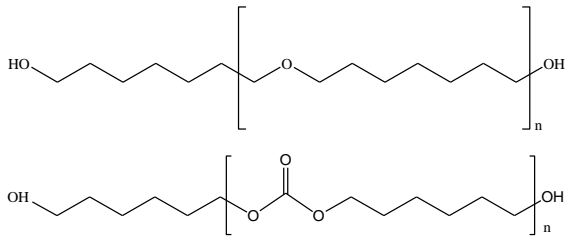
- ➔ Introduction
- ➔ **Experimental**
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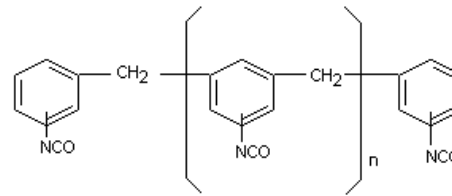


## SYNTHESIS OF PU's

➔ 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)**

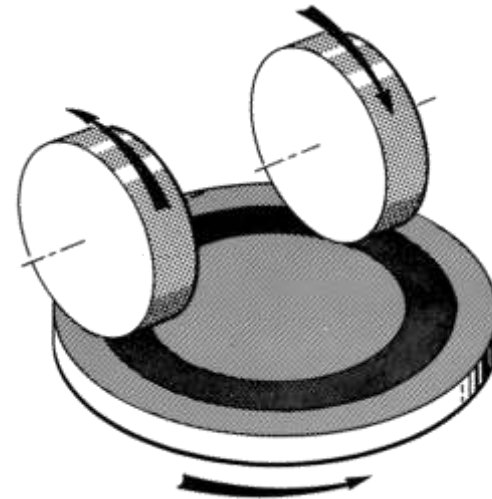


**1,4-butanediol**

**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

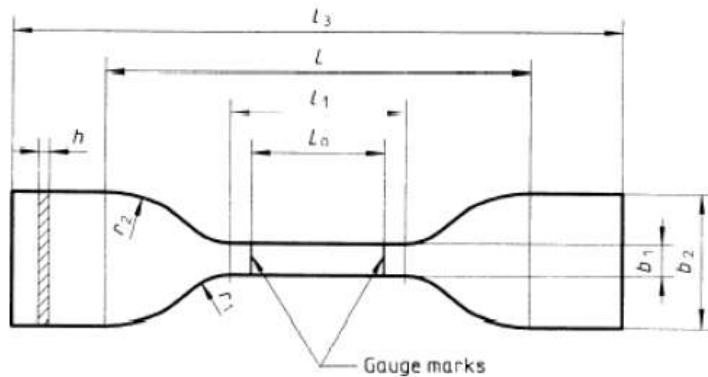


**Universal Testing Machine Instron 4411  
Instron Corp.  
(Norwood, MA, USA)**

## EXPERIMENTAL TECHNIQUES

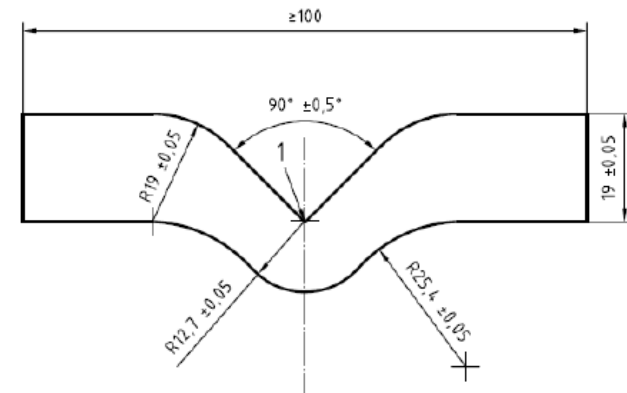
### ➔ Mechanical properties

#### STRESS - STRAIN



ISO 37-2:2005

#### TEAR STRENGTH



ISO 34-1:2004



## EXPERIMENTAL TECHNIQUES

### ➔ Hydrolysis resistance: ASTM D471

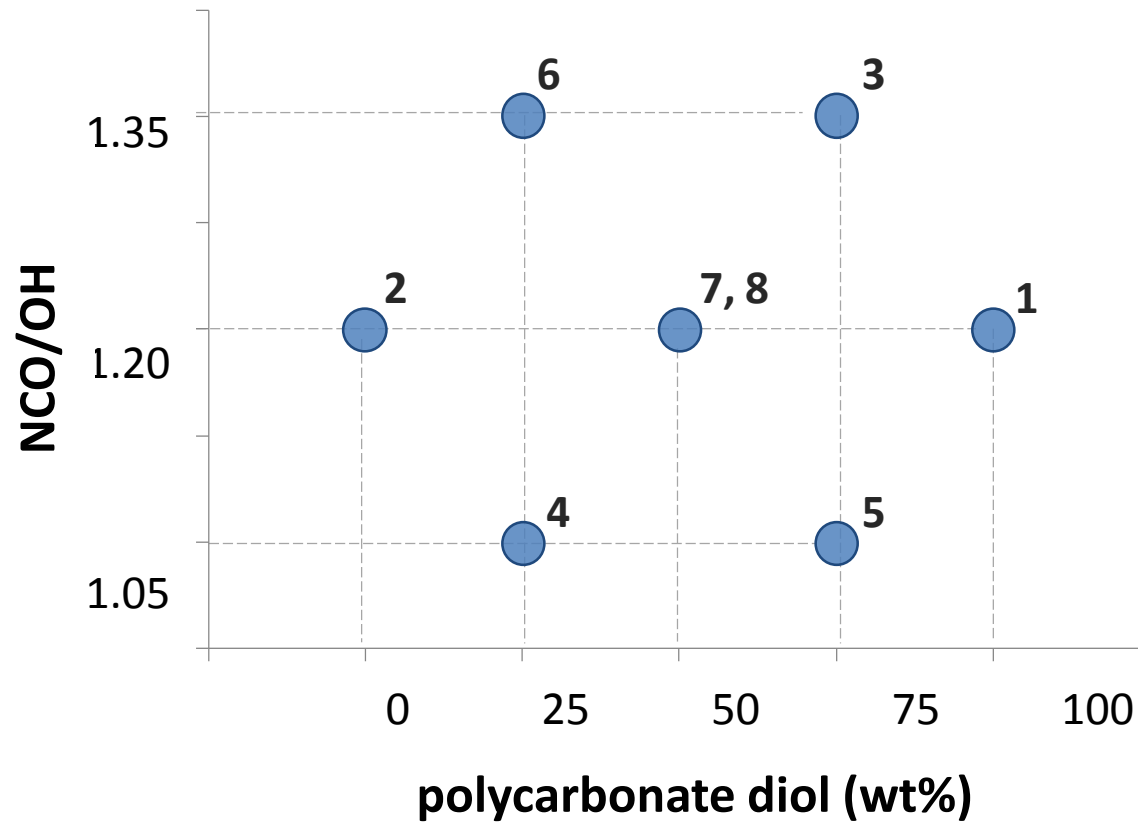
Soaking specimens of polyurethanes in water at 70°C for 500 hours

## 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

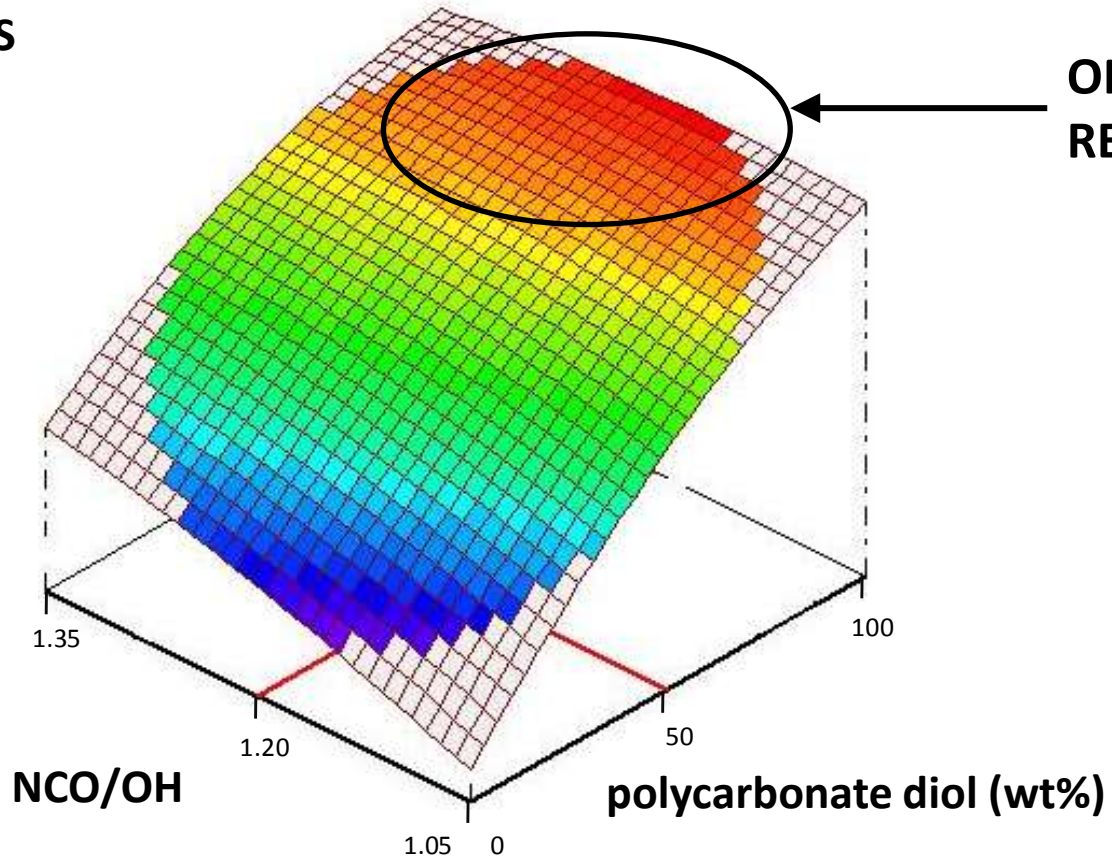
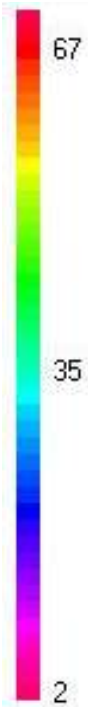


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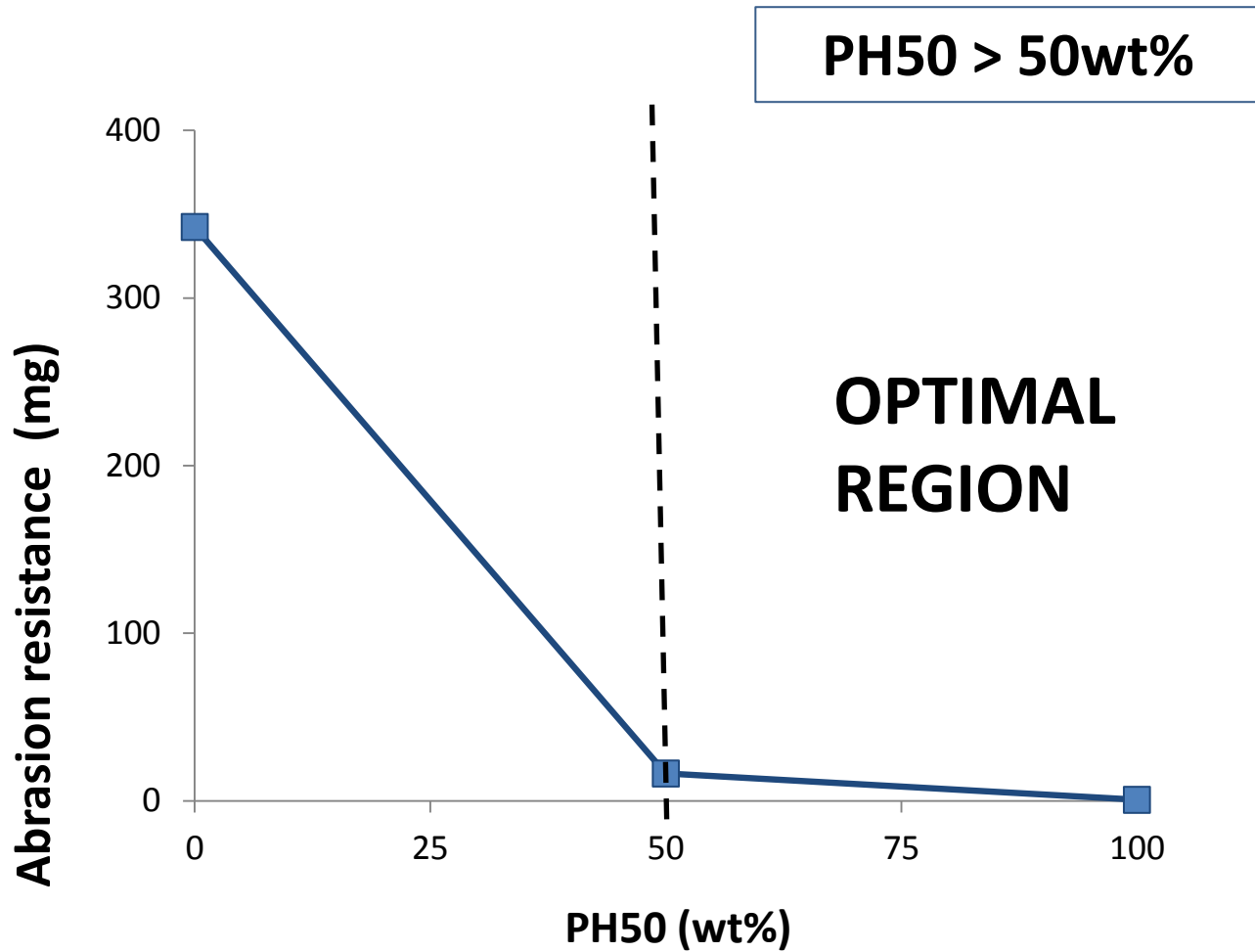
Formulation	Pot life (min)	Viscosity (mPa · s)	Abrasion resistance (mm <sup>3</sup> )
Specification	10 -16	< 2000	< 50 mm
Polycarbonate diol-free blank	on spec	on spec	34
PH50-including optimization	13.5	870	4

- **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



OPTIMAL REGION

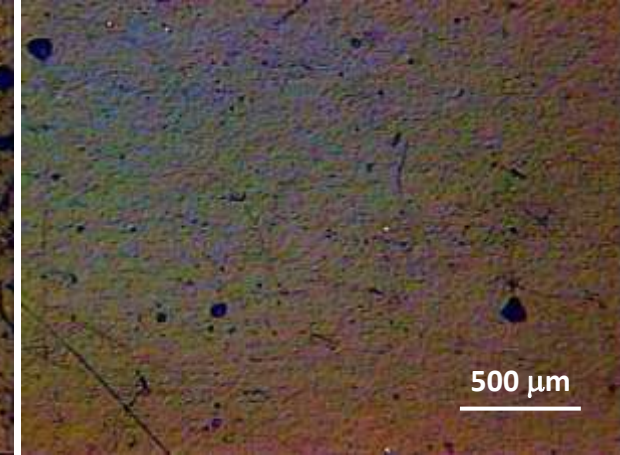
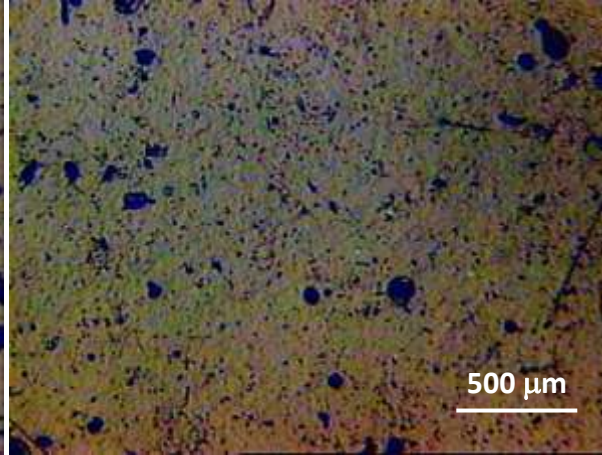
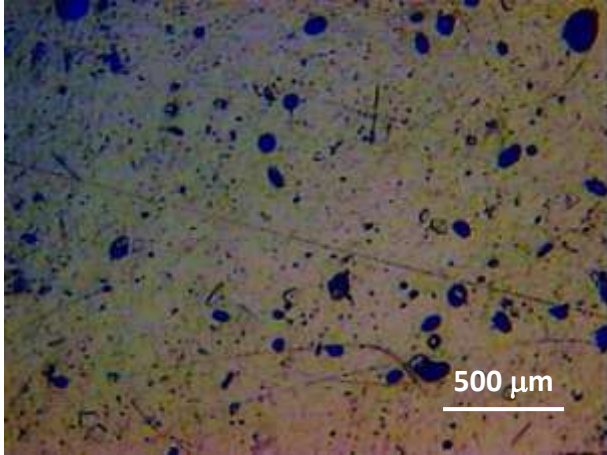


100wt% PTMG

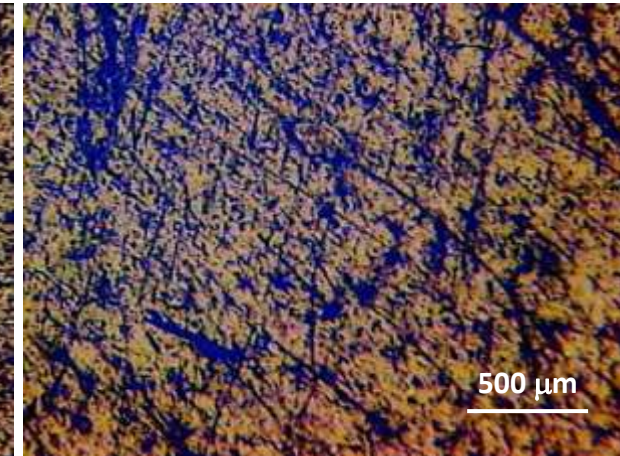
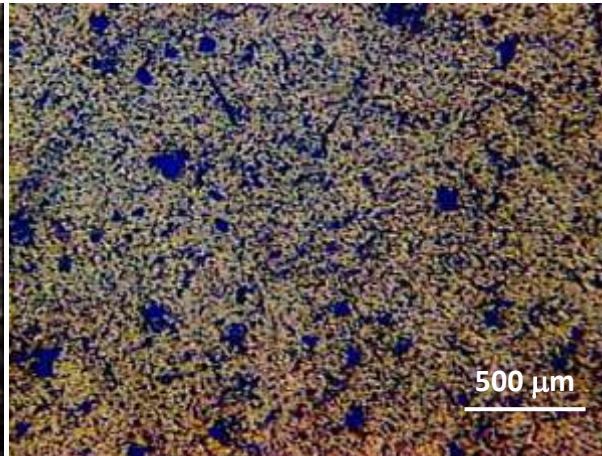
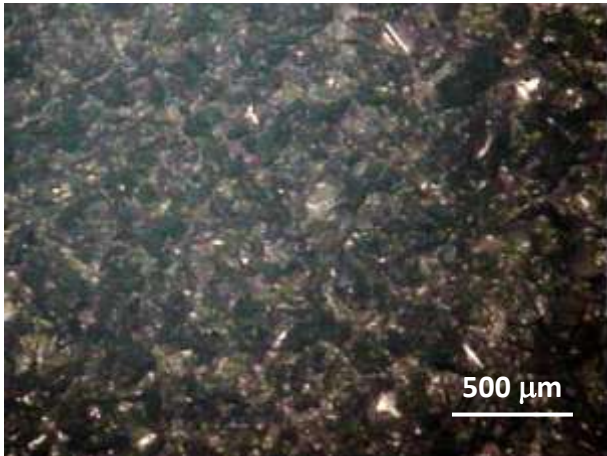
50wt% PTMG + 50wt%  
polycarbonate diol

100wt%  
polycarbonate diol

**Before abrasion**



**After abrasion**





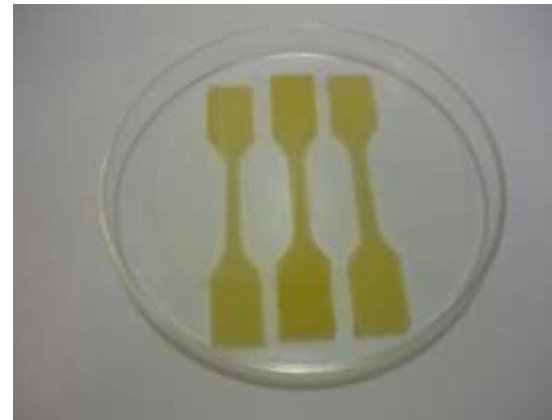
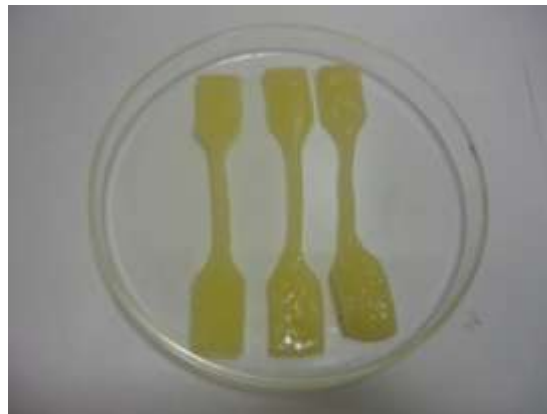
100 wt% PTMG

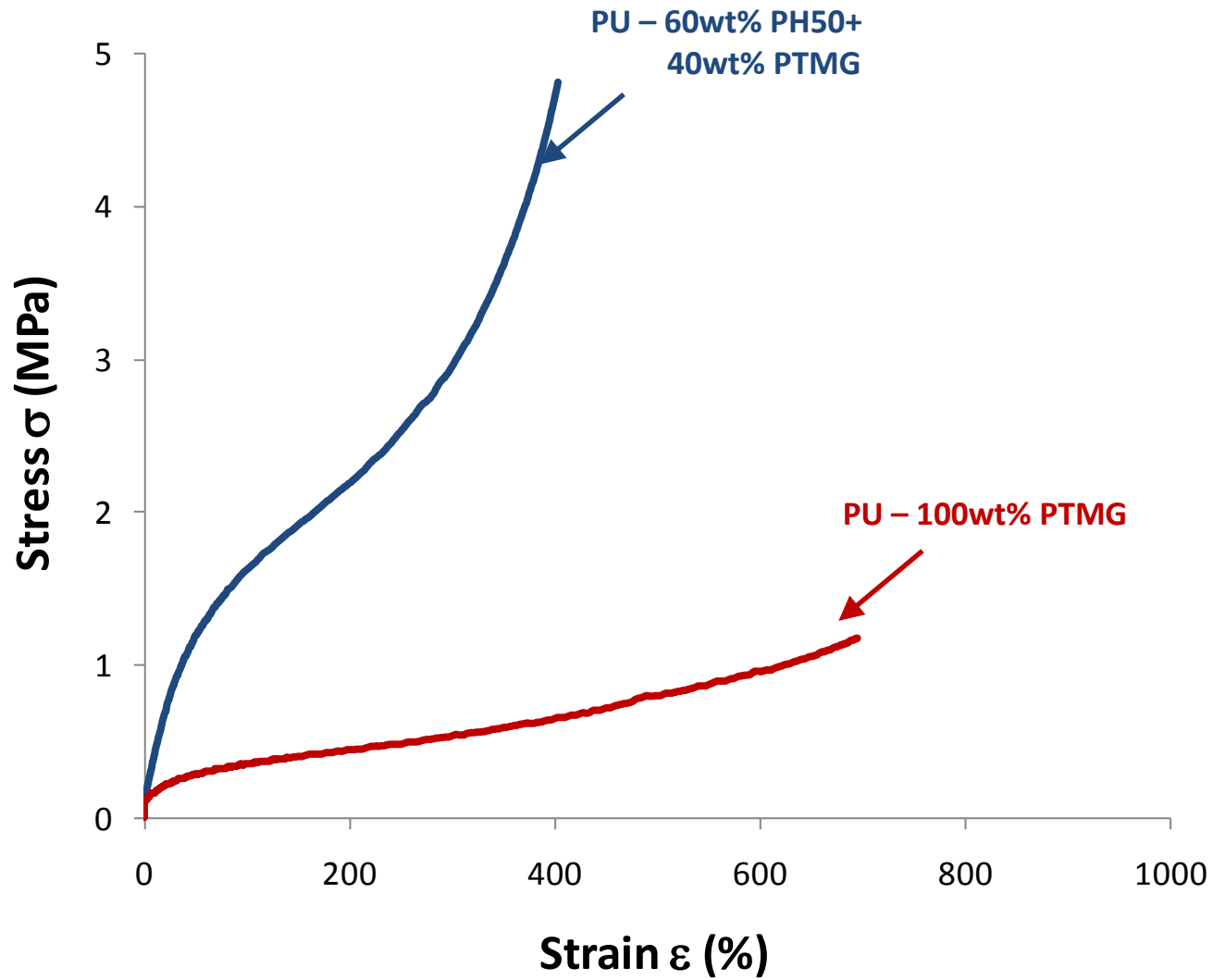
60 wt% PH50 +  
40 wt% PTMG

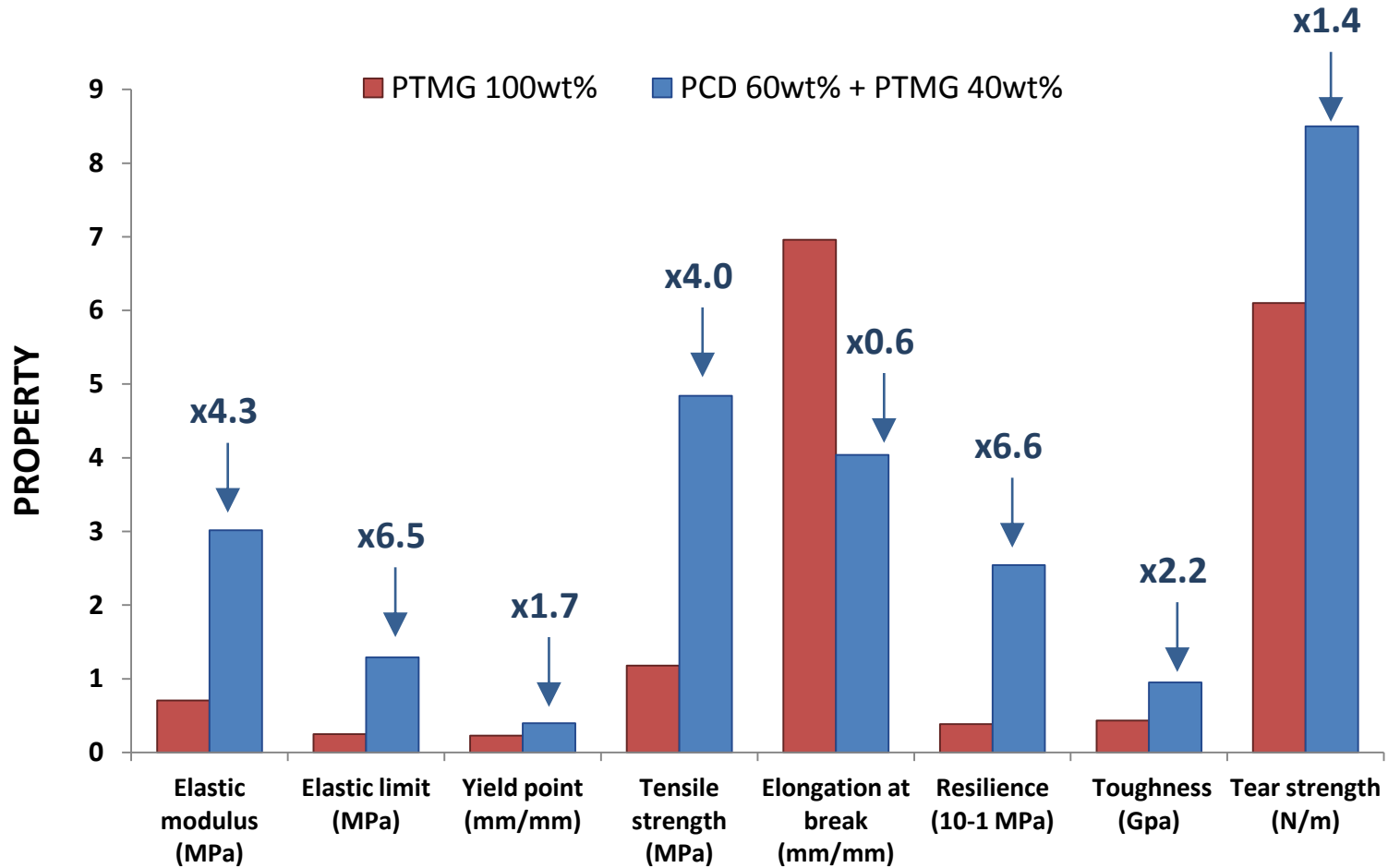
Before ageing

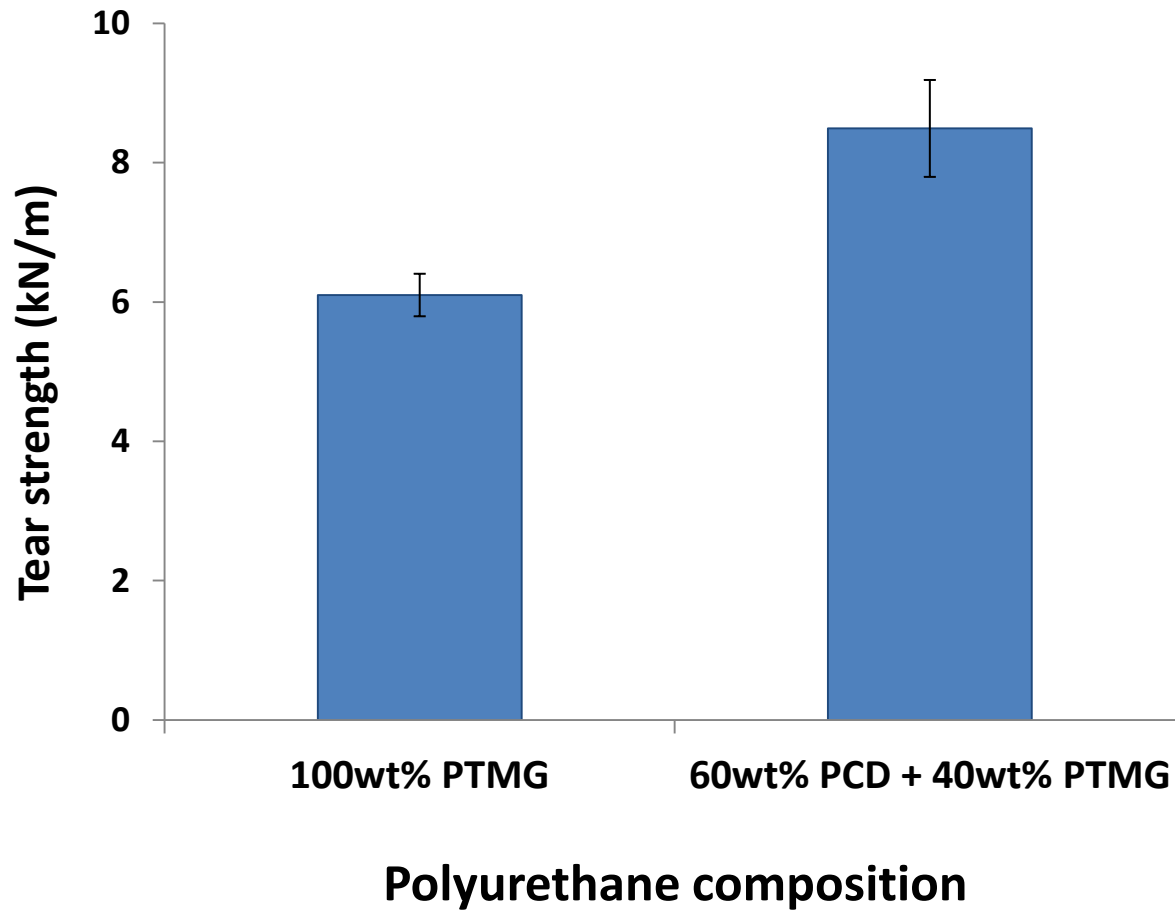


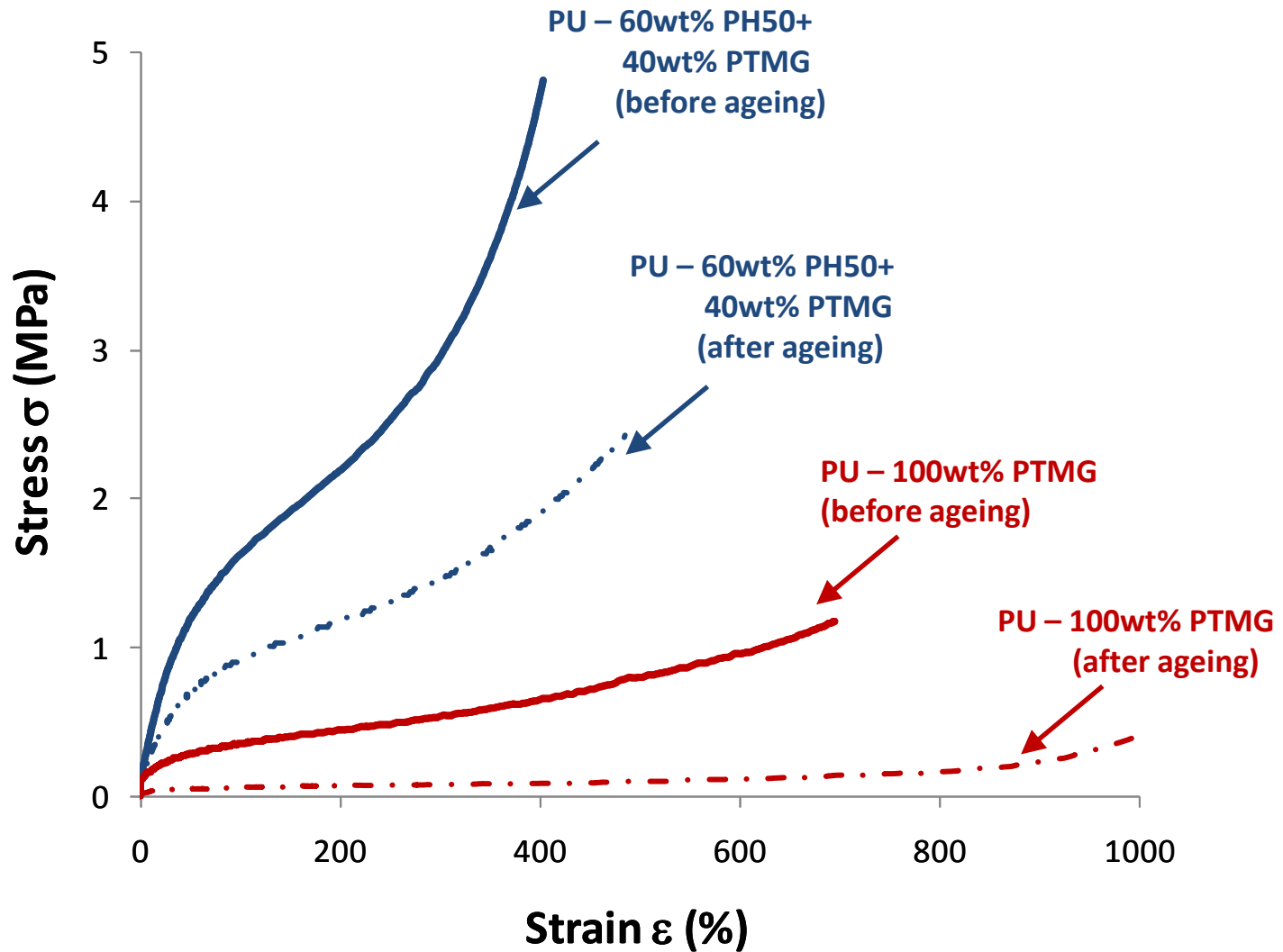
After ageing

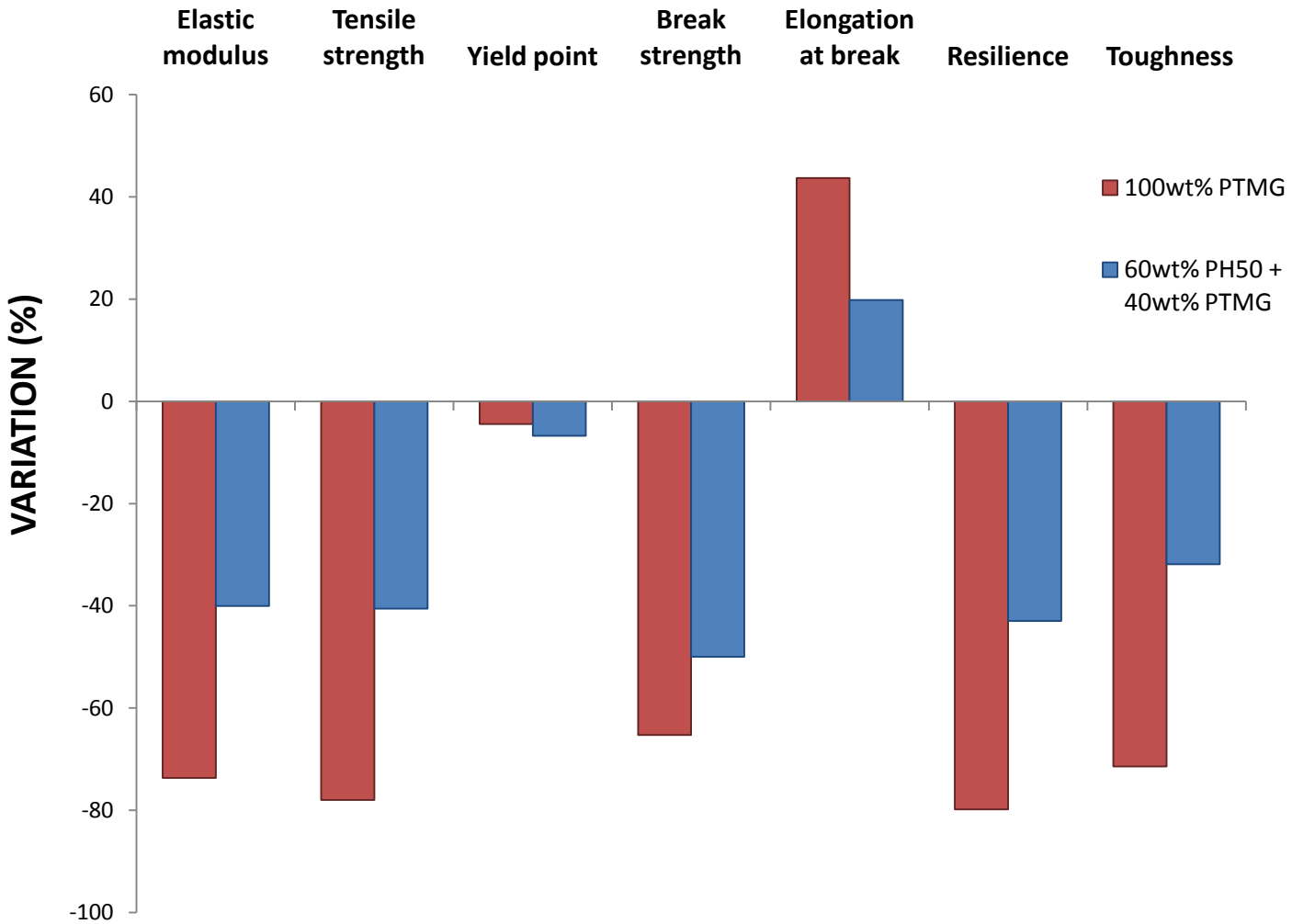


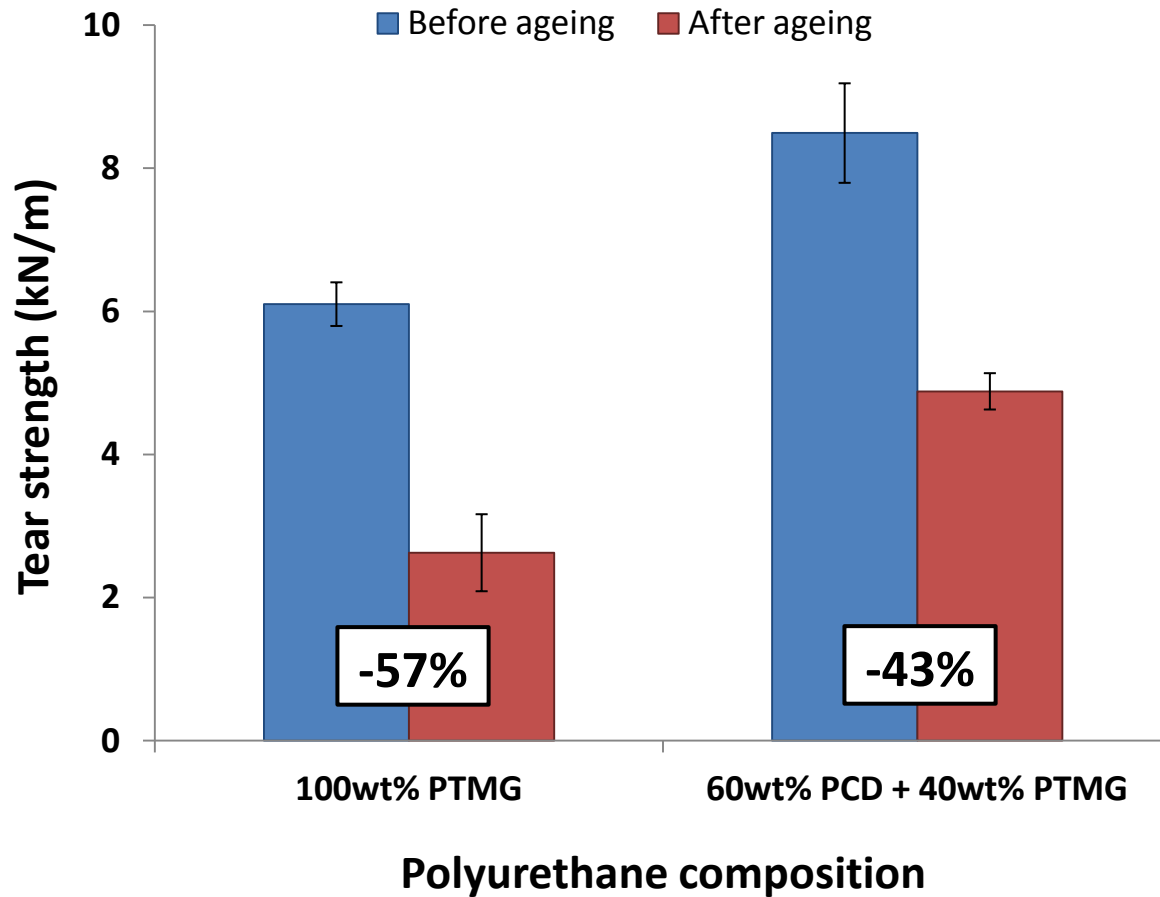












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- ➔ Addition of polycarbonate diol produced a huge improvement in the mechanical properties of polyurethanes
- ➔ PU coating losses by abrasion can be minimized by using polycarbonate diol content higher than 50 wt% in the polyol
- ➔ PU coatings containing polycarbonate diol showed high hydrolytic stability and less losses of properties after hydrolytic 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](http://www.ube.es)
- ✓ Envie um e-mail a [d.Hernandes@ube.ind.br](mailto:d.Hernandes@ube.ind.br)
- ✓ Fale com Daniel Hernandez – 11 9 6640 6053