

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

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- **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)

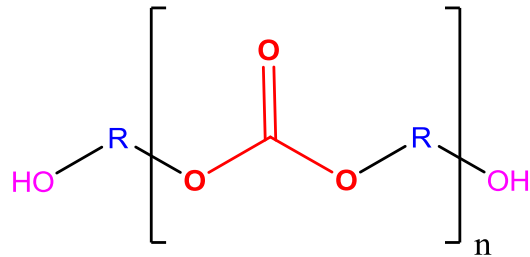
H. Song, Z. Zhang, X. Men, Z. Luo. «***A study of the tribological behavior of nano-ZnO-filled polyurethane composite coatings***» Wear 269 (1-2), 79-85 (2010)

- ➔ **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.

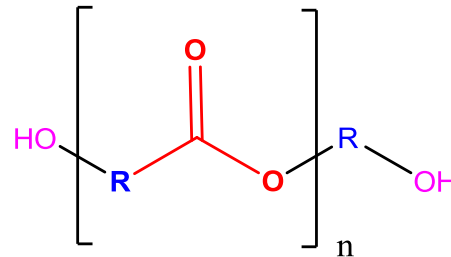
V. García-Pacios, M. Colera, Y. Iwata, J.M. Martín-Martínez.
«Incidence of the polyol nature in waterborne polyurethane dispersions on their performance as coatings as stainless steel» Progress in Organic Coatings 276 (12), 1726-1729 (2013)

Terminal – Backbone – Bridge – Backbone – Terminal



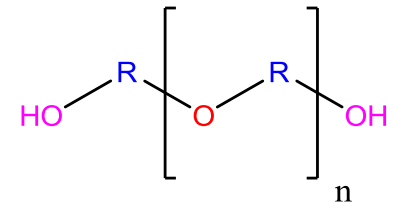
Polycarbonate diol

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







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

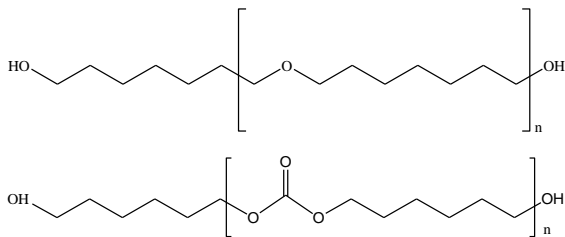
- Improve the mechanical properties and abrasion resistance

- Improve the durability of internal PU coatings for pipelines by using polycarbonate diol in their synthesis

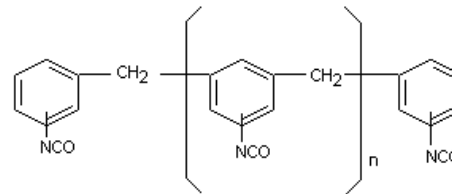
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SYNTHESIS OF PU's

➔ **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)**

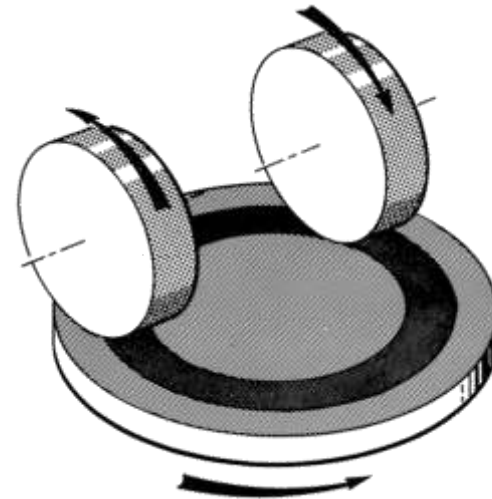


1,4-butanediol

**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

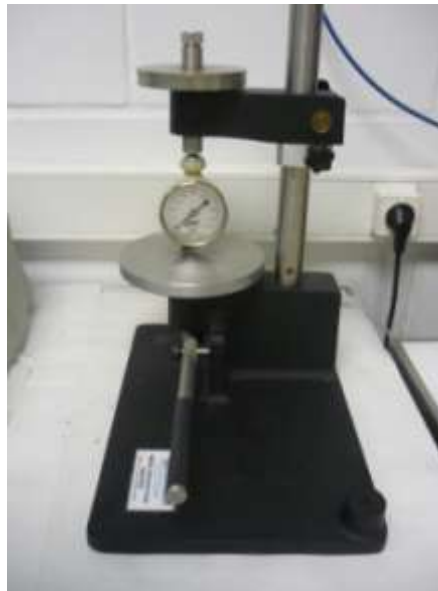
➔ Optical microscopy



**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

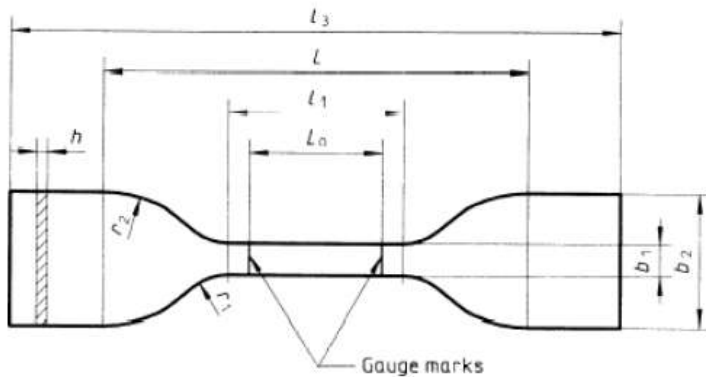


**Universal Testing Machine Instron 4411
Instron Corp.
(Norwood, MA, USA)**

EXPERIMENTAL TECHNIQUES

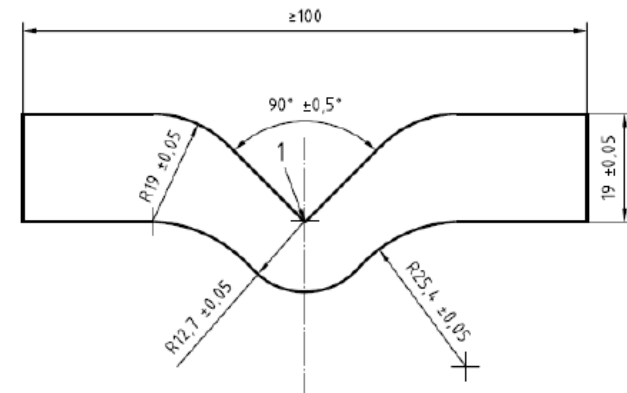
➔ Mechanical properties

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

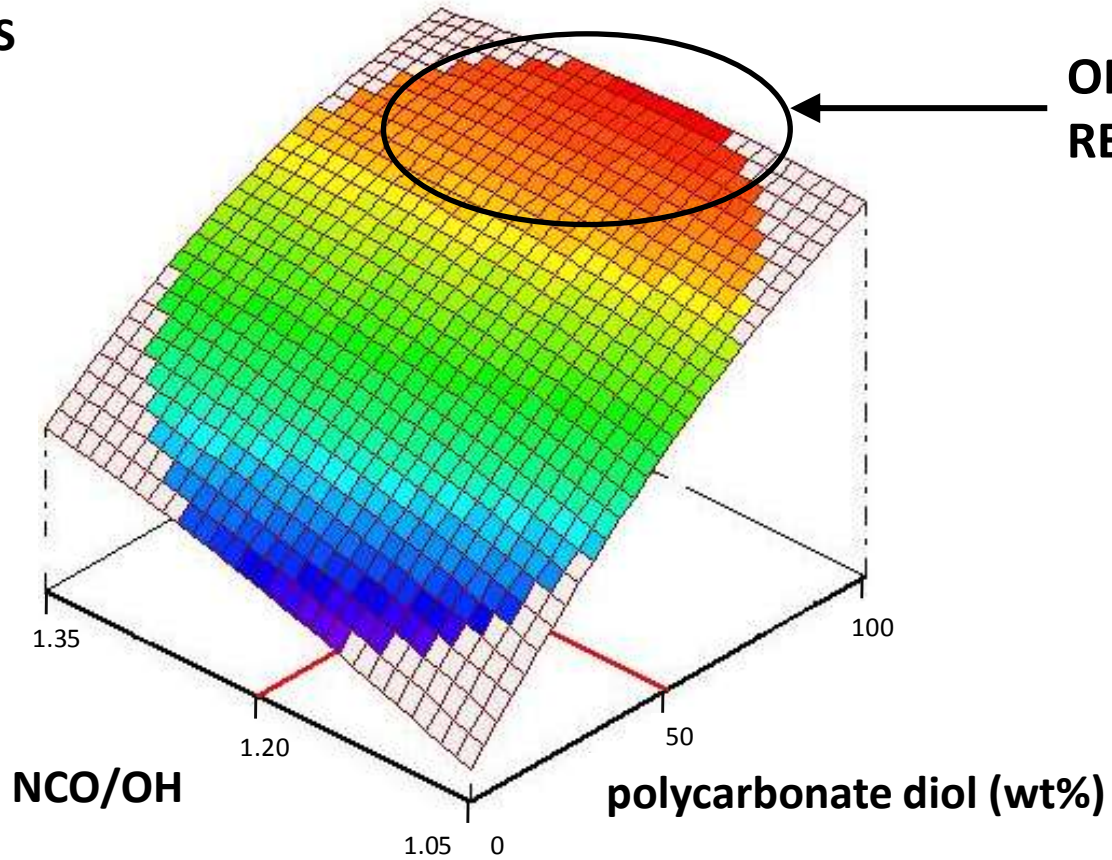
- ➔ **Use of experimental design approach to study different variables simultaneously**
- ➔ **Variables to study:**
 - ✓ **Weight content of polycarbonate diol in the polyol mixture of polyether + polycarbonate diol**
 - ✓ **NCO/OH ratio**

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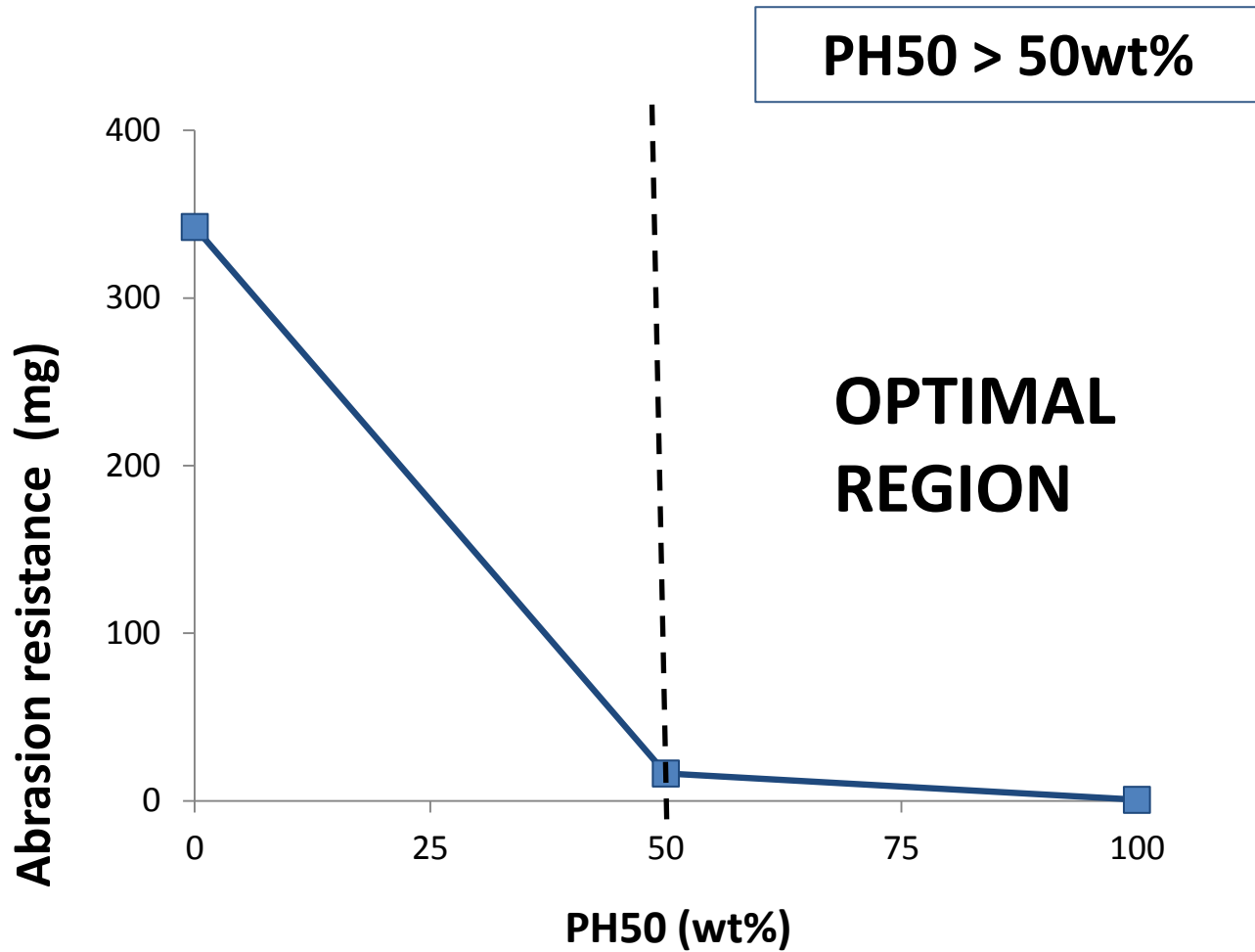
Formulation	Pot life (min)	Viscosity (mPa · s)	Abrasion resistance (mm ³)
Specification	10 -16	< 2000	< 50 mm
Polycarbonate diol-free blank	on spec	on spec	34
PH50-including optimization	13.5	870	4

- **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



OPTIMAL REGION

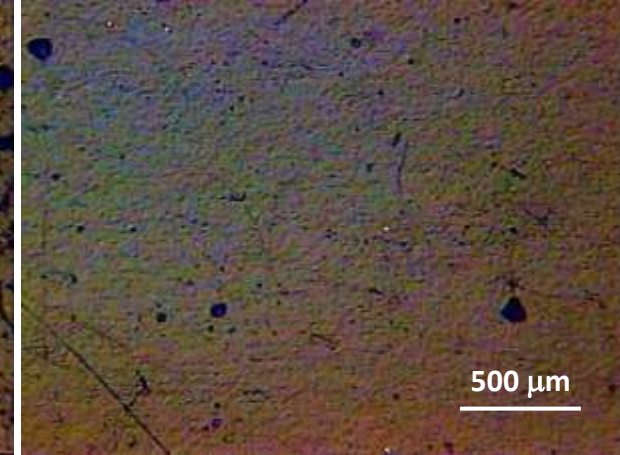
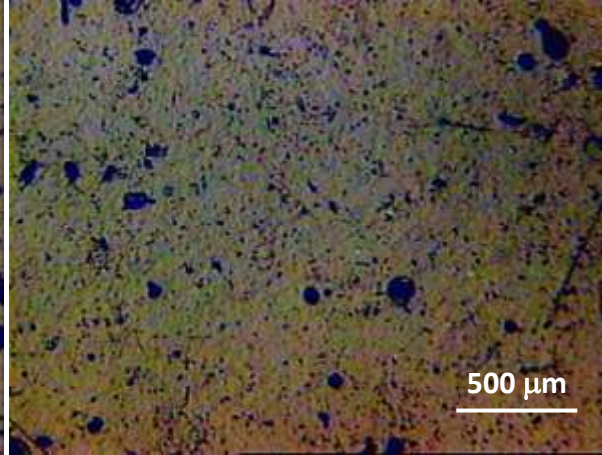
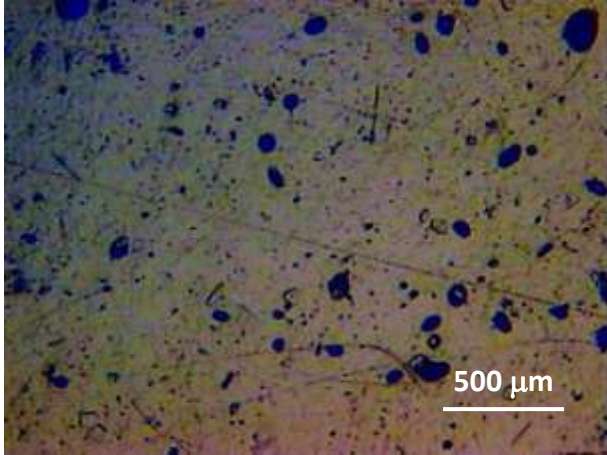


100wt% PTMG

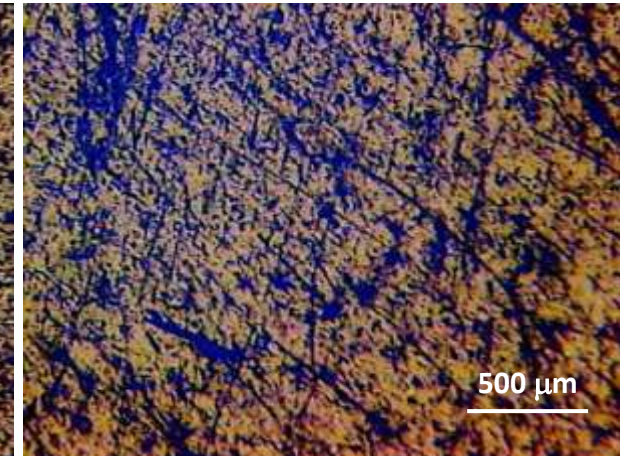
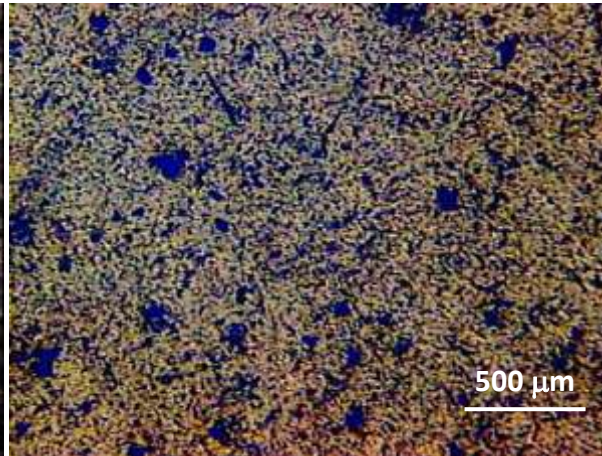
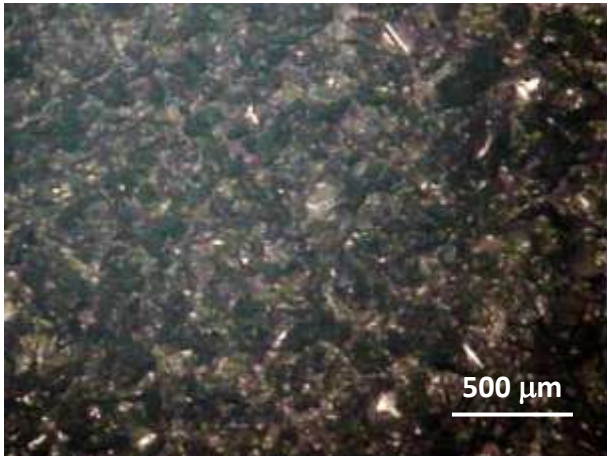
50wt% PTMG + 50wt%
polycarbonate diol

100wt%
polycarbonate diol

Before abrasion



After abrasion



Before ageing

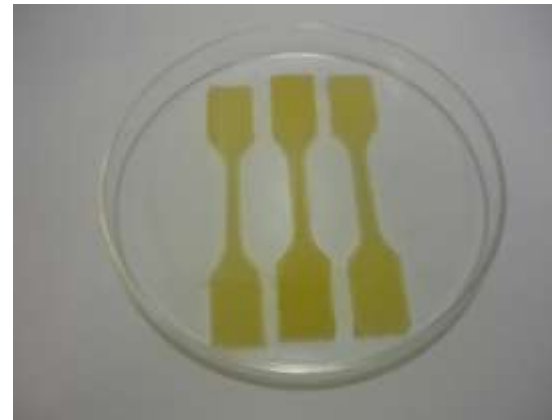
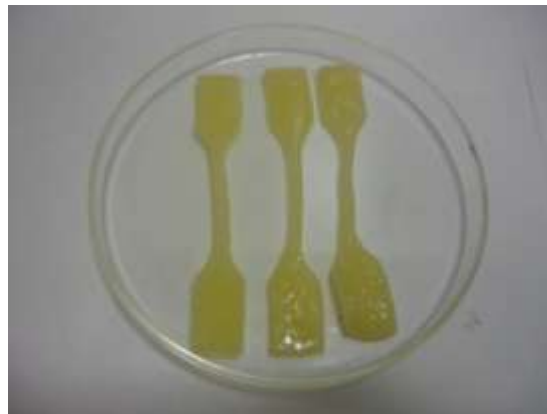
100 wt% PTMG

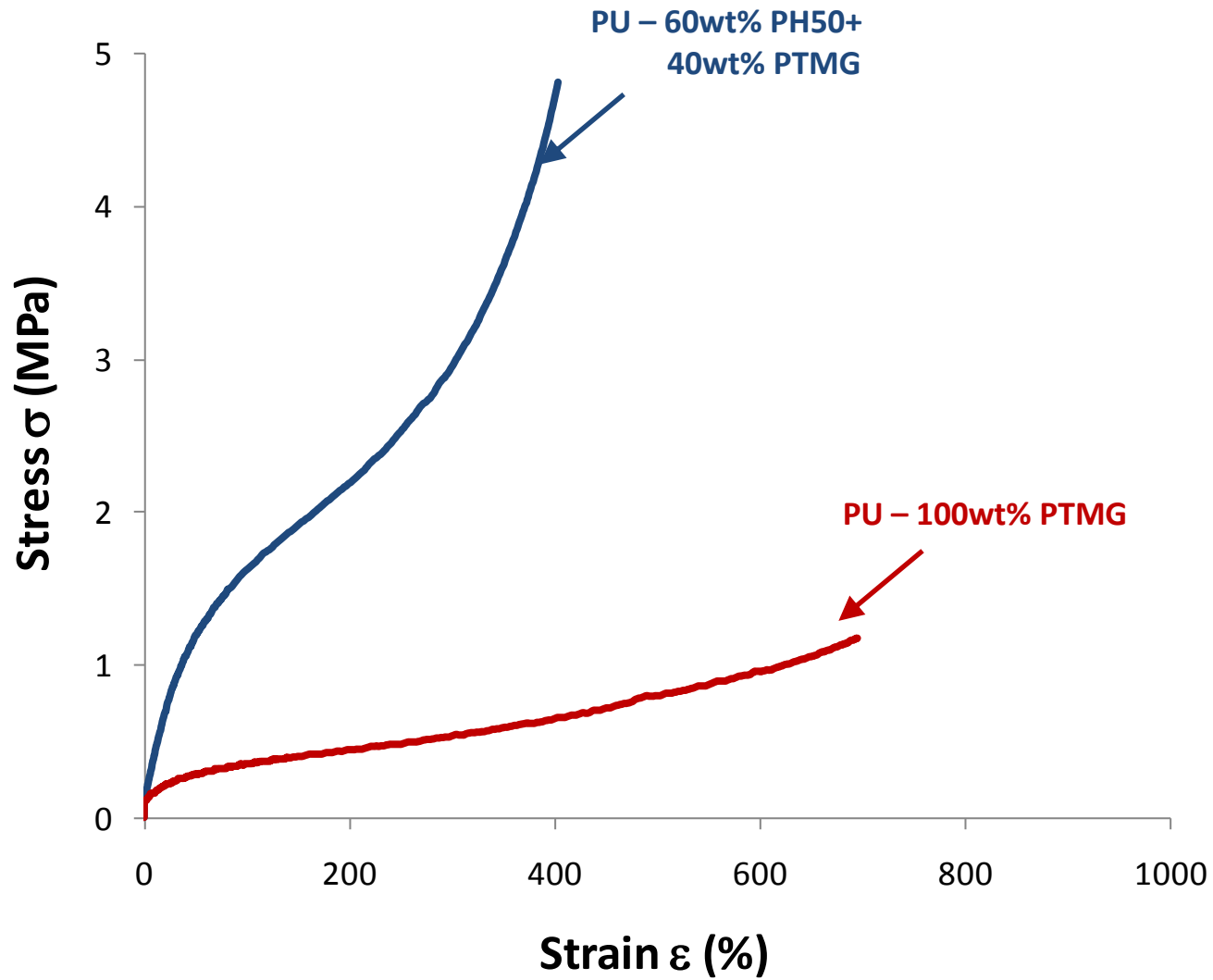


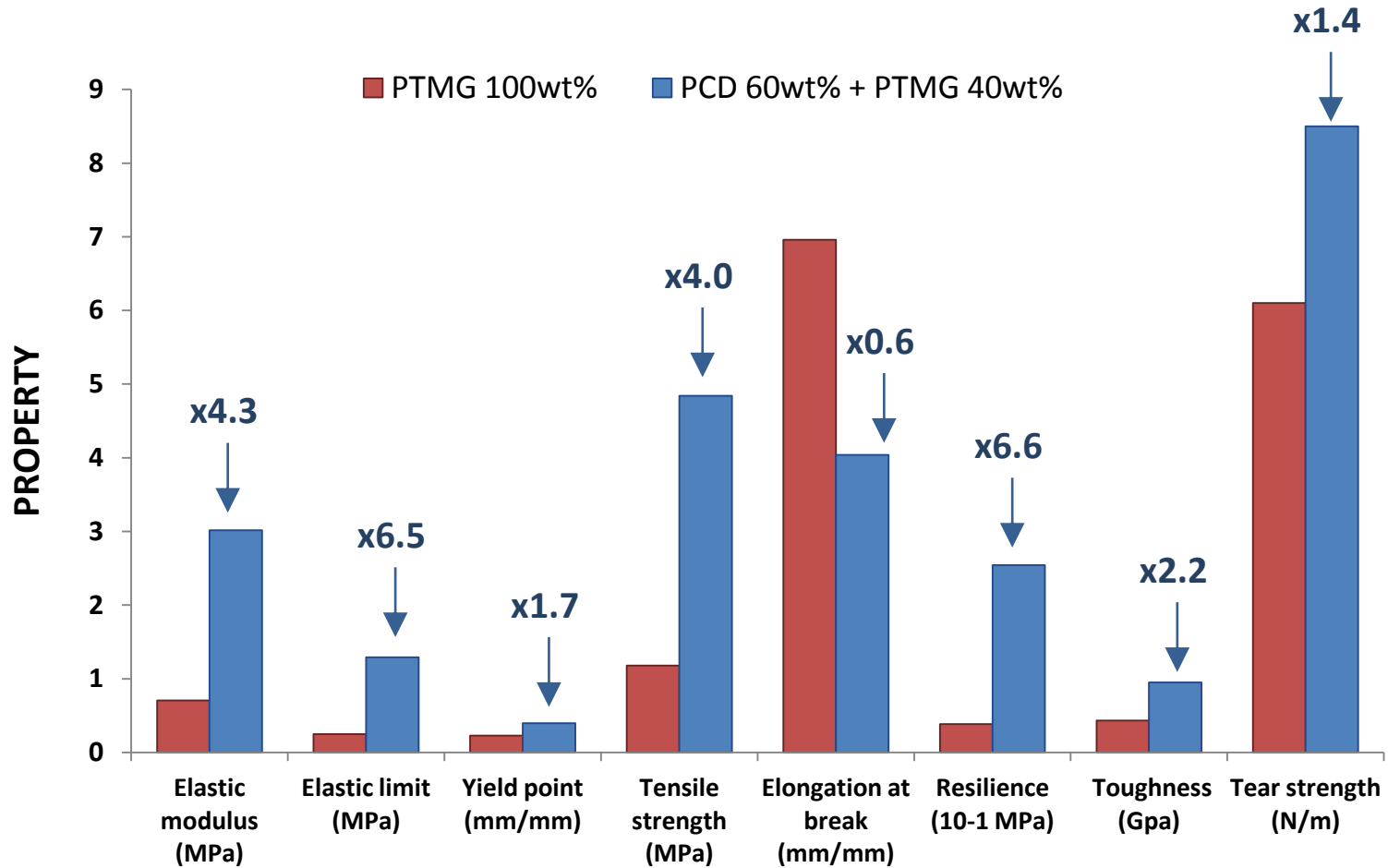
60 wt% PH50 +
40 wt% PTMG

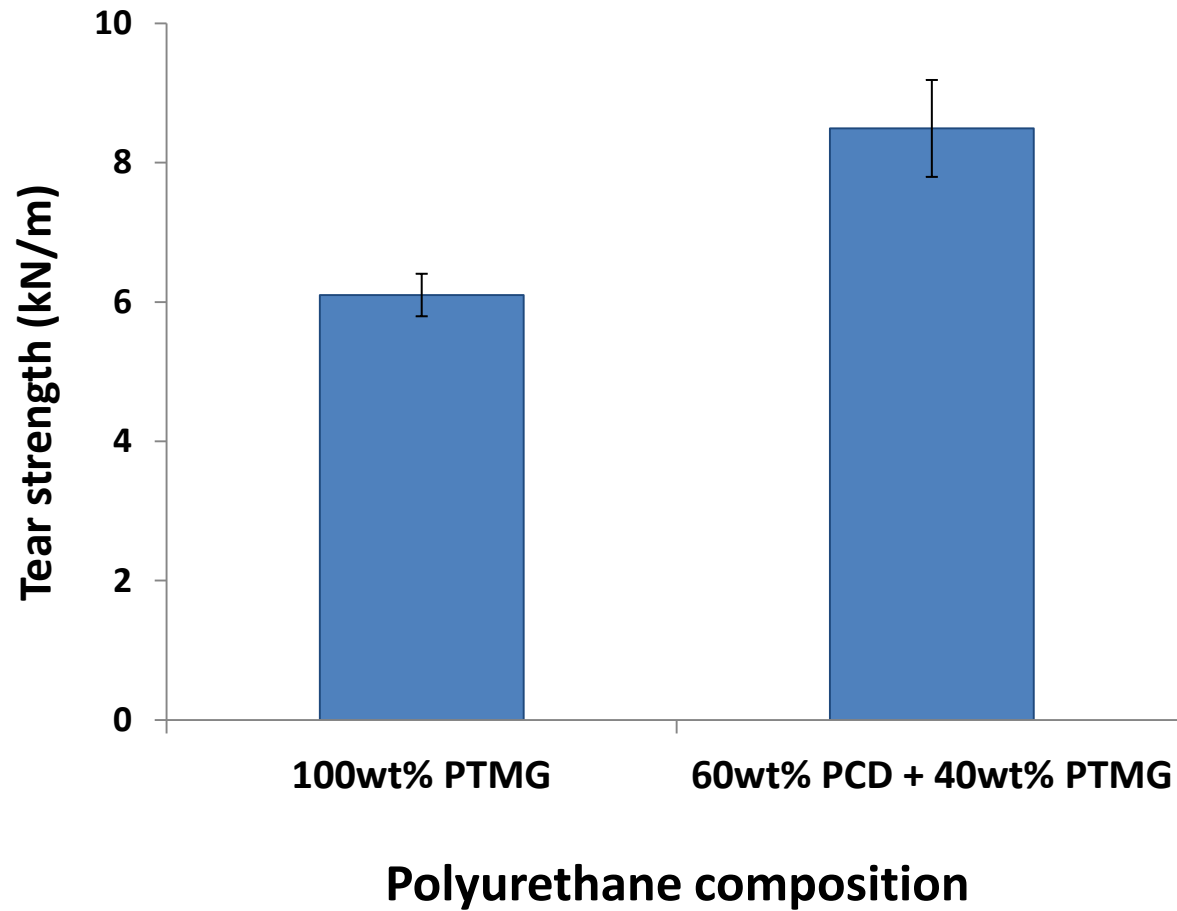


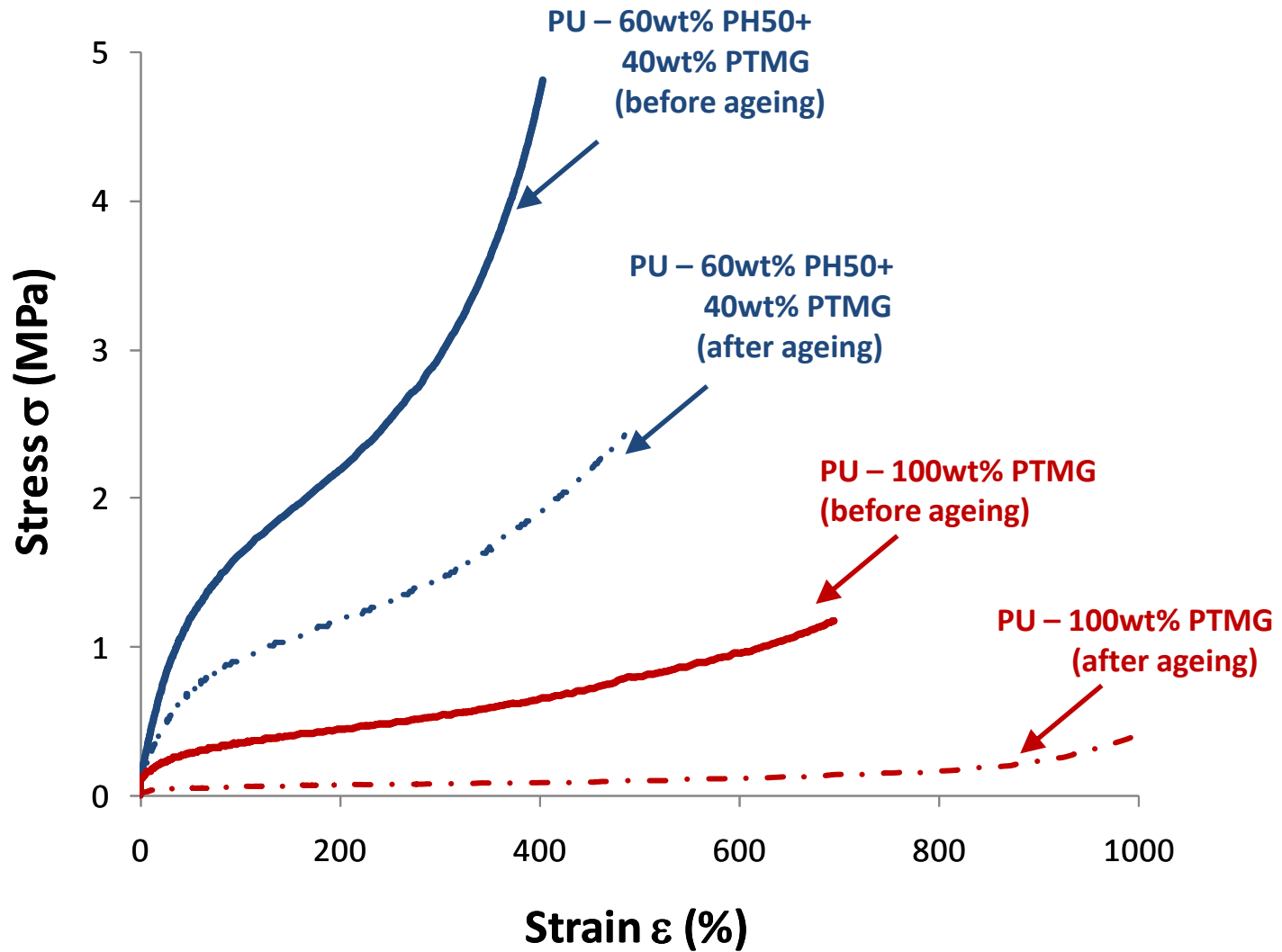
After ageing

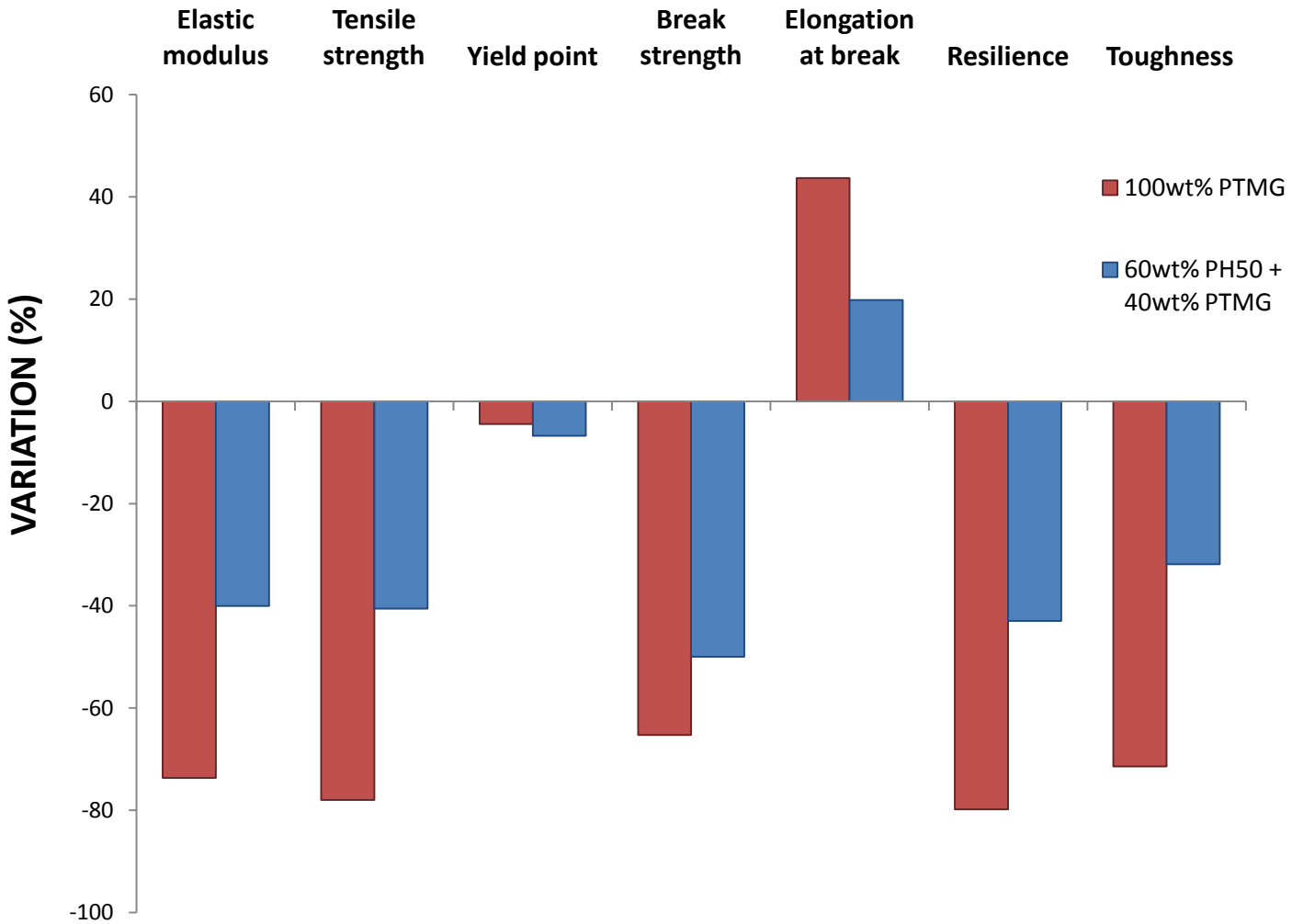


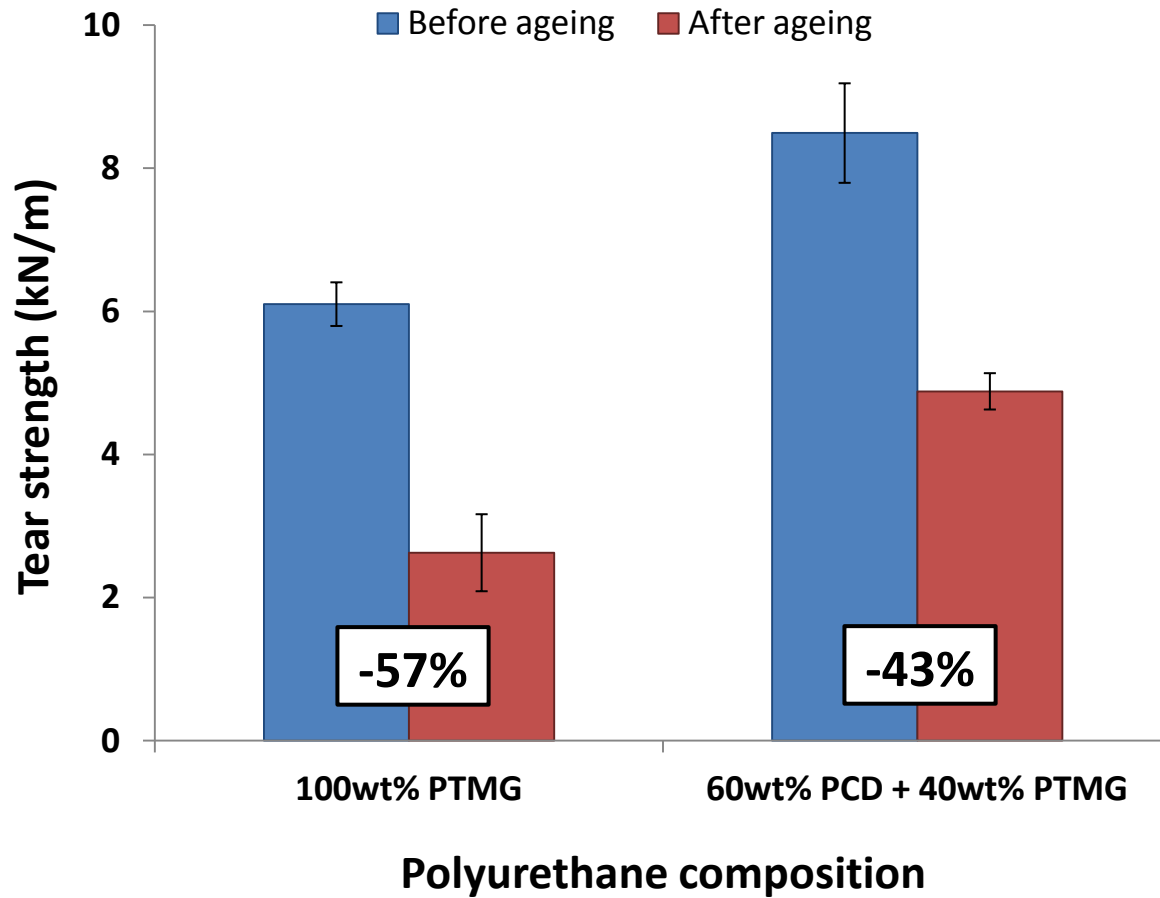












- ➔ Introduction
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- ➔ Addition of polycarbonate diol produced a huge improvement in the mechanical properties of polyurethanes
- ➔ PU coating losses by abrasion can be minimized by using polycarbonate diol content higher than 50 wt% in the polyol
- ➔ 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.com*
- ✓ *Envie um e-mail a f.mantovani@ube.ind.br*
- ✓ *Fale com Fernando Mantovani – 11 9 7609-5811*