Improving Polyurethane durability by choosing the UBE PCD: Elastomers and Coatings

General presentation November – 2012

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RESPONSIBLE CARE
El Compromiso de la Industria Química con el Desarrollo Sostenible

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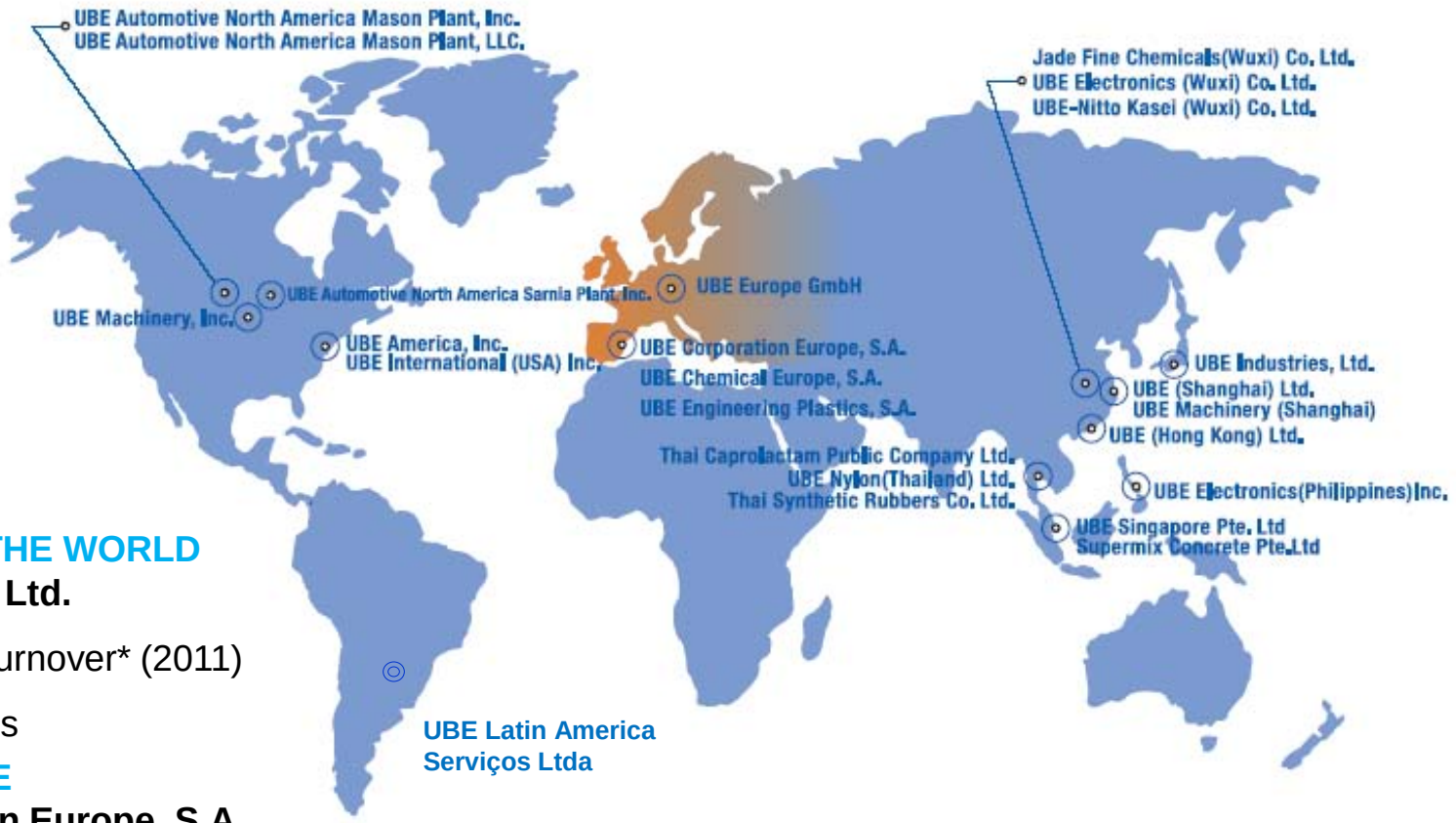
Introduction UBE company



UBE AROUND THE WORLD

UBE Industries, Ltd.

Billion € 5,835. turnover* (2011)

11.026 employees

UBE IN EUROPE

UBE Corporation Europe, S.A.

384 M€ turnover (2011)

370 employees (2011)

UBE product line

- Specialty Chemicals & Products

  Specialty Products (Polyimides, Battery materials, Separation membranes, Ceramics)

  Fine Chemicals (DMC, Diols, PCD, diphenol derivatives)

  Pharmaceuticals

- Chemicals & Plastics

  Caprolactam

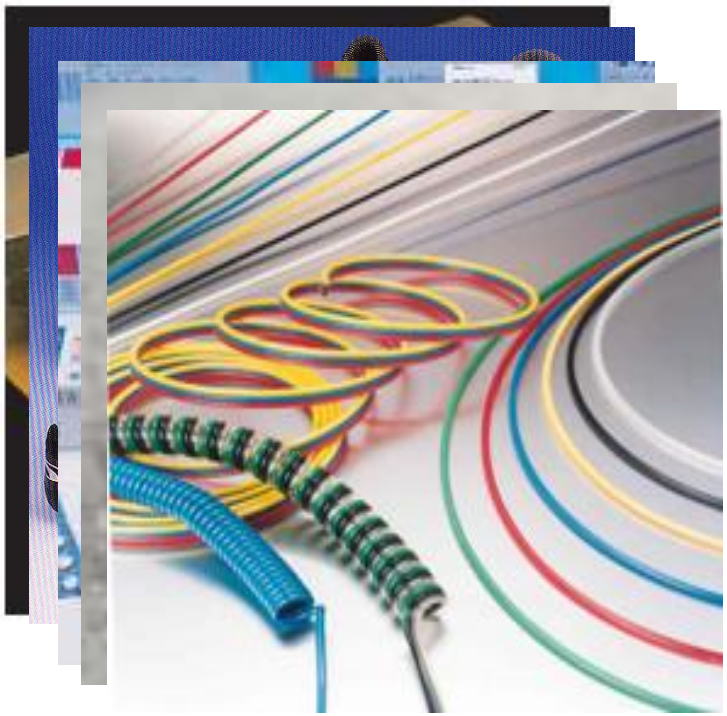
  Polyamides

  Synthetic Rubber

- Cement & Construction Materials

- Machinery and Metal Products

- Energy and Environment



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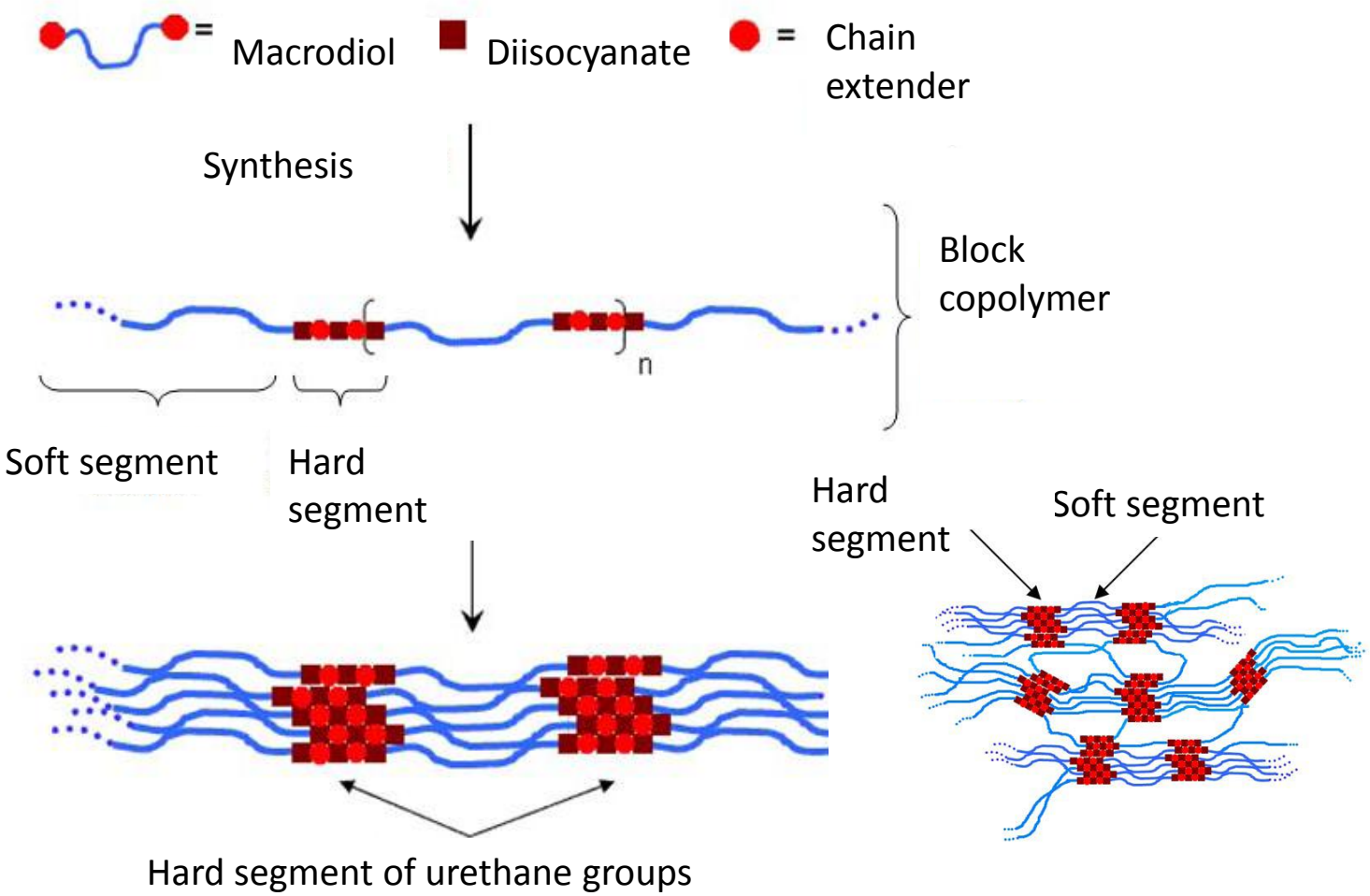
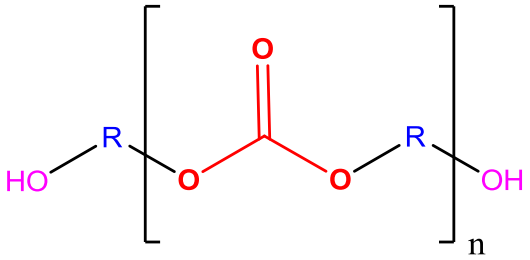
Synthesis

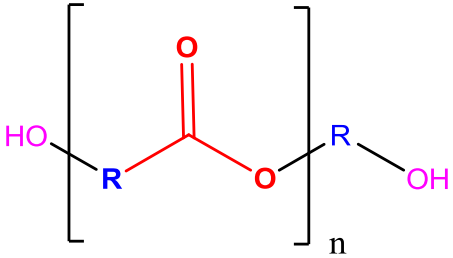


Polyols structures

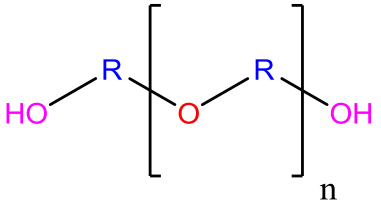
Terminal – Backbone – Bridge – Backbone – Terminal



Polycarbonate diol



Polyester diol



Polyether diol

Polyurethane **mechanical properties** can be defined by using an optimum backbone (***R***) or by different molecular weight (**n**)

Durability properties:

Carbonate vs. ester & ether as bridge:

- Higher hydrolysis
- Higher chemical resistance
- Excellent stain resistance
- Better heat & weather resistance

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TPU – Elastomers: Cooperation with ICMUV (University of Valencia)

Synthesis:

Polyol: BuDL : MDI = 1 : 2 : 3 molar (Two-shot process)

T = 80ºC and P = atmospheric in Argon

Residence time = 3h to 5h

Solid content = 22%wt (Solvent DMA)

Hard segment content = 48 %

Films:

Thin Film applicator NEURTEK RK → 0,2 mm thickness

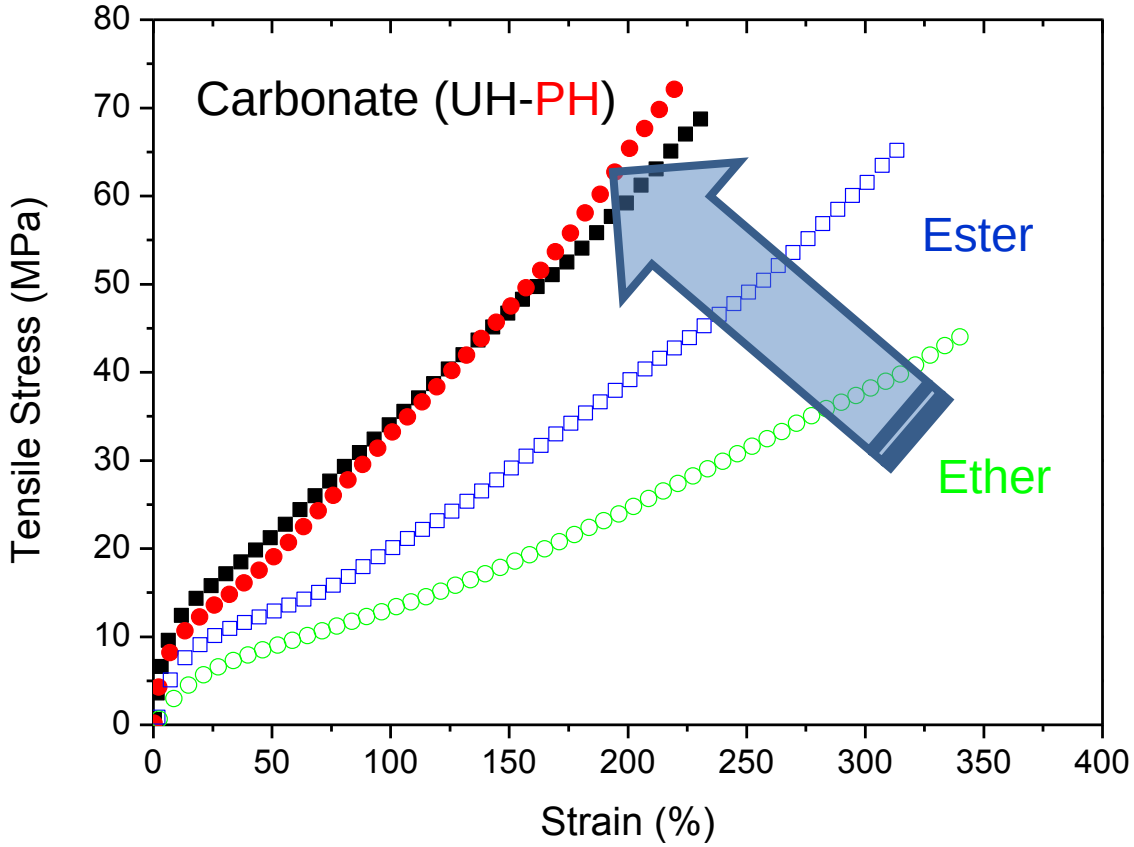
Drying 80ºC for 24 h

Mechanical properties

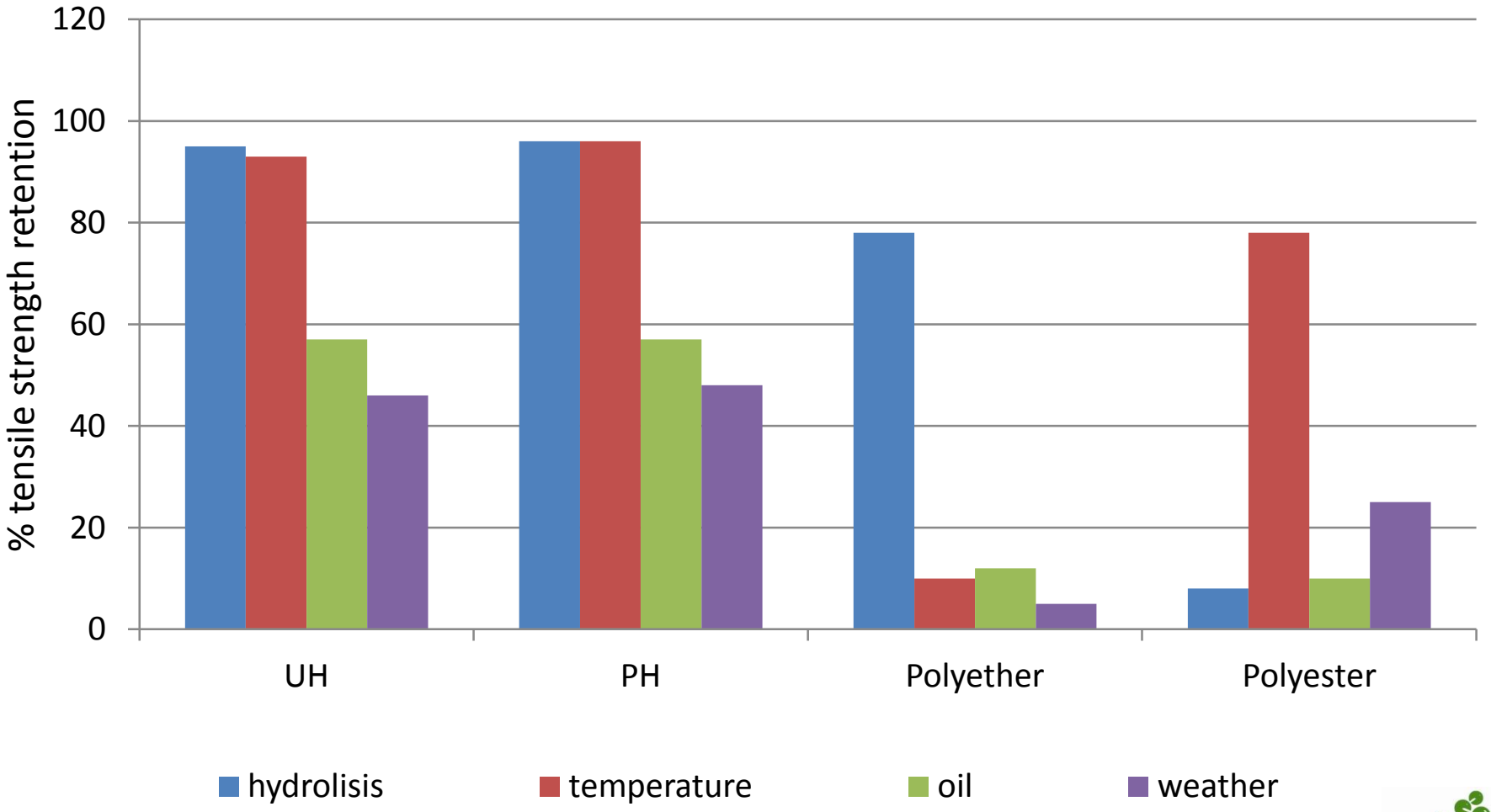
Properties	UH-100	PH-100	POLYESTER	POLYETHER
Density (g/cm^3)	1.20	1.22	1.25	1.11
Hardness (Shore A)	92	89	93	83
Modulus elongation 100% (Mpa)	34	34	20	13
Modulus elongation 200% (MPa)	60	66	40	23
Tensile strength(Mpa)	70	75	69	41
Elongation at break (%)	231	222	323	345
Tear strength (MPa)	168	154	123	92
Glass transitions	31	26	2	7

POLYESTER = 1,4-BUTANEDIOL ADIPATE
POLYETHER = POLYPROPYLENE GLYCOL

TPU: Mechanical properties



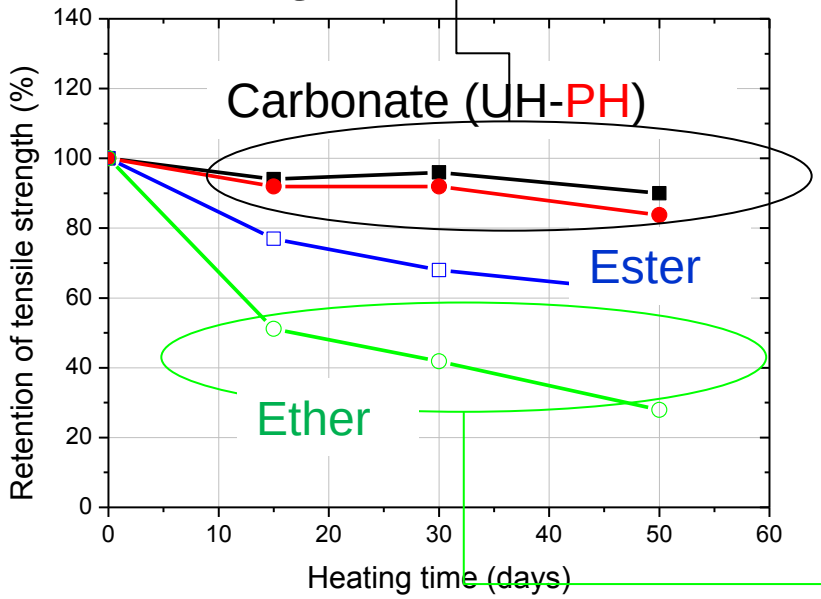
Degradation Resistance of TPU

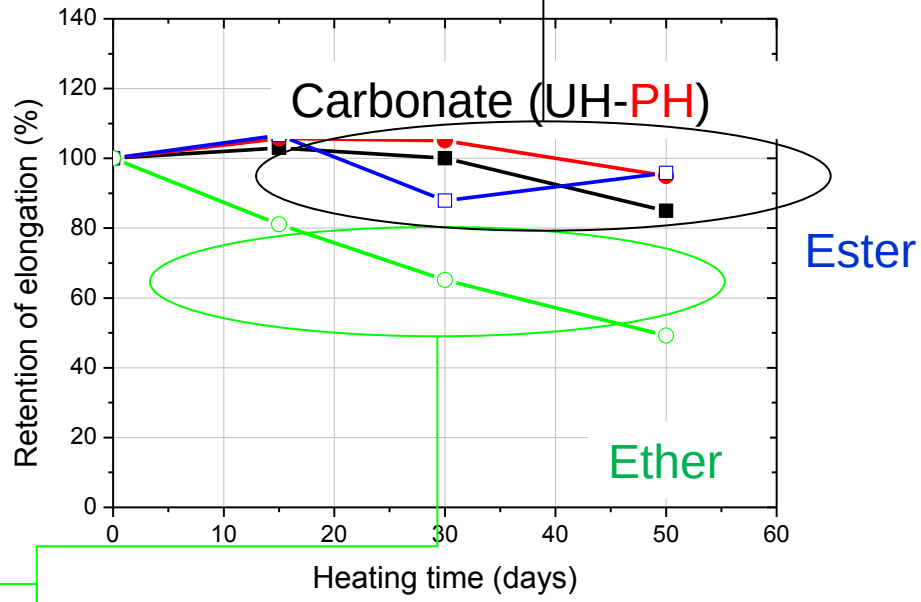


TPU: Heating resistance at 120 ºC

TPU-PCD excellent:

Heating resistance



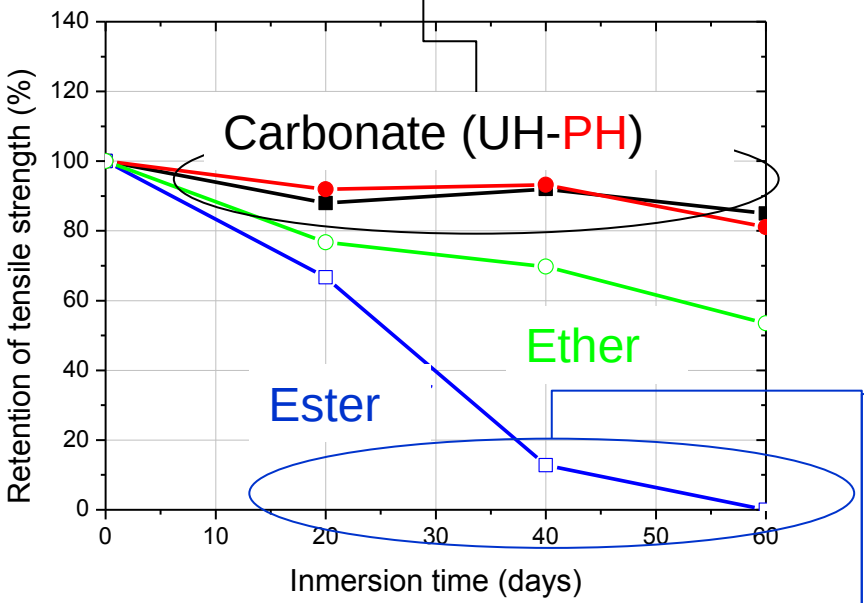


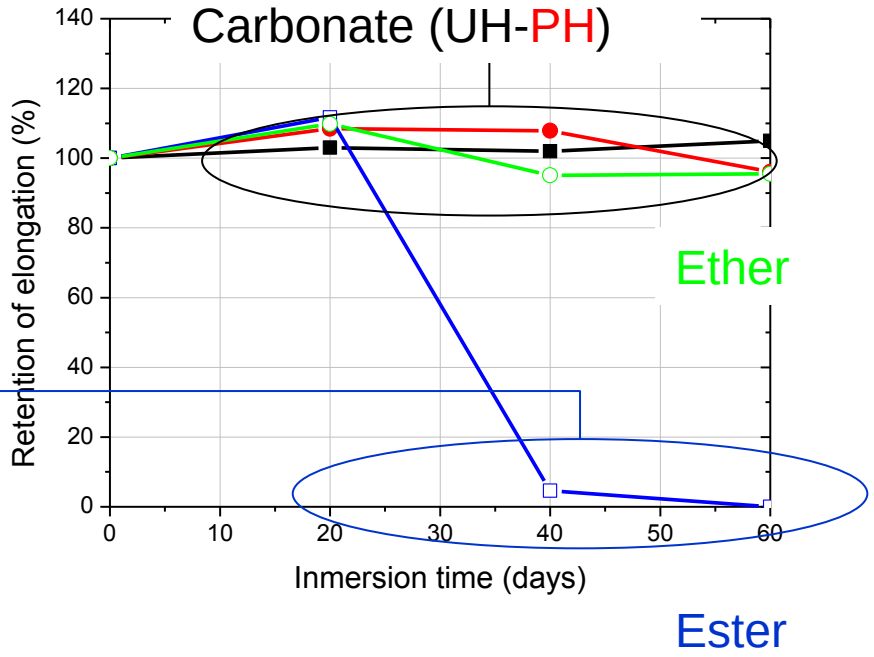
TPU-Polyether very poor:
Heating resistance

TPU: Hydrolysis resistance in water at 80 ºC

TPU-PCD excellent:

Hydrolytic resistance



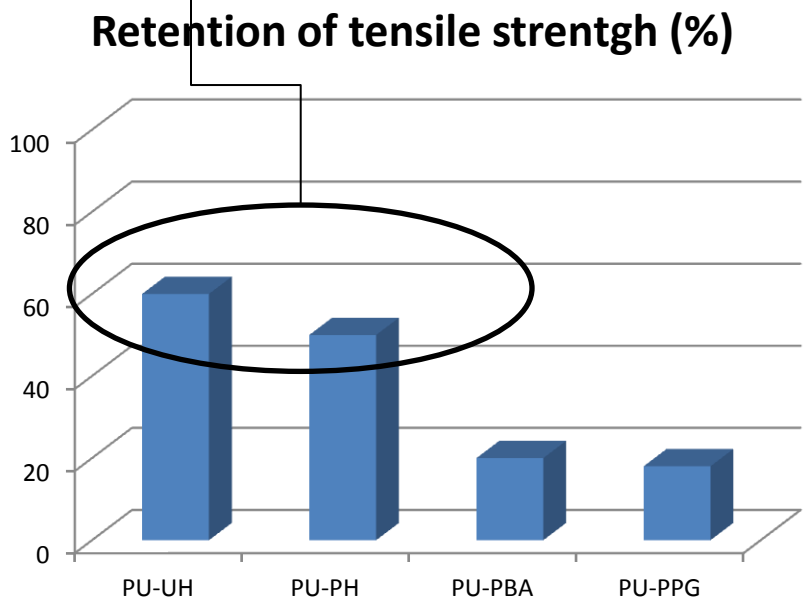


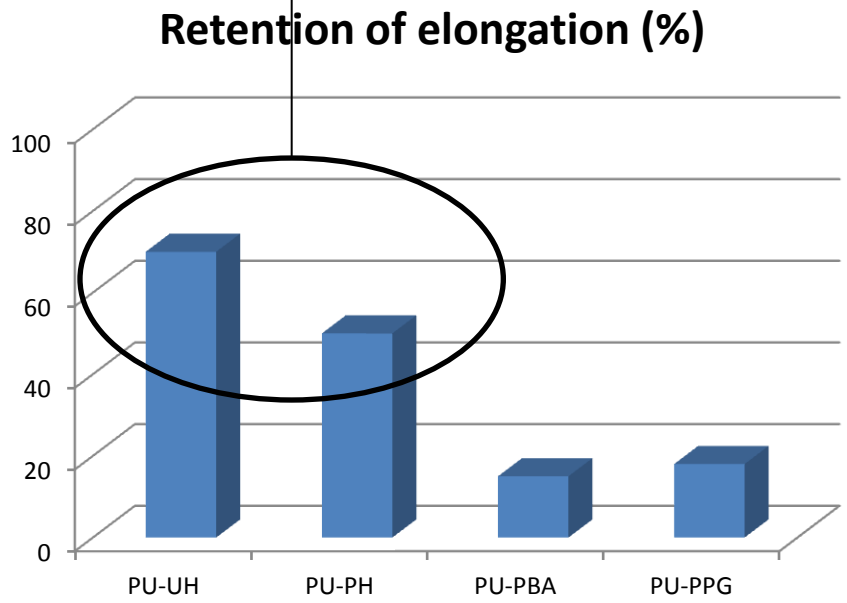
TPU-Polyester very poor: water resistance

TPU: Weather Resistance

TPU-PCD excellent:

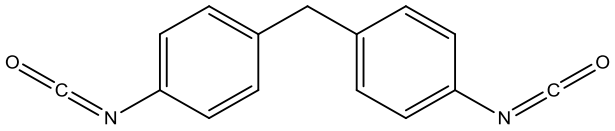
weather resistance





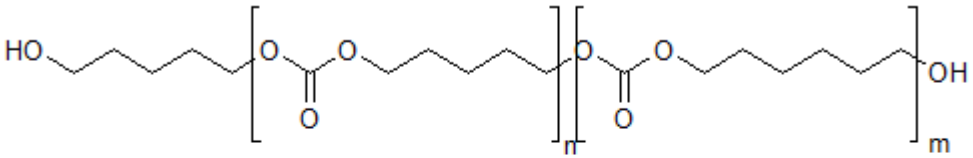
Weather conditions:
λ= 340 nm borosilicate filters,
Radiation of 35 W m^2 nm,
T= (65±3) ˚C.
Dry cycle of 102 min continuous by 1 min of spray water (raining simulation).

Raw materials

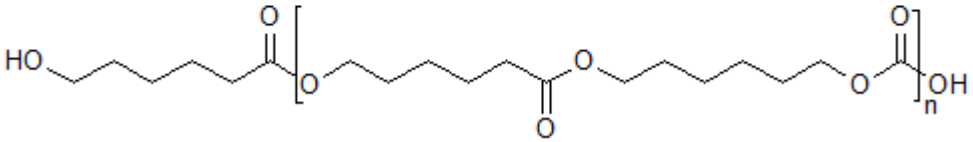


MDI

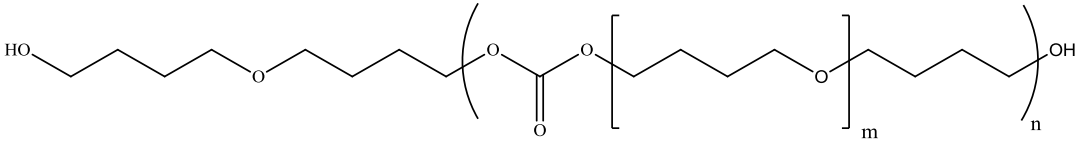
Butanediol



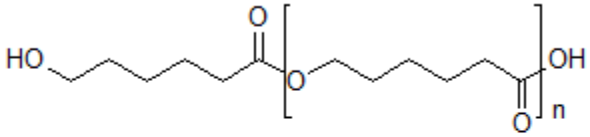
PH
(PCD)



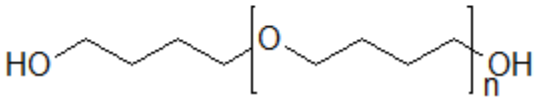
UHC
(polyester &PCD)



UT
(polyether & PCD)



PCL
(polyester)



PTMG
(polyether)

Method TPU elastomers

System	Molar ratio macrodiol: MDI:BDL	Hard segment content (wt%)
PUPH100-48	1:3:2	48
PUPH200-32	1:3:2	32
PUUHC100-48	1:3:2	48
PUUHC200-32	1:3:2	32
PUUT200-32	1:3:2	32
PUPTMG100-48	1:3:2	48
PUPTMG200-32	1:3:2	32
PUPCL100-48	1:3:2	48
PUPCL200-32	1:3:2	32

Synthesis:

✓Two-shot process in 100% solid content .

✓T = 70 ºC and atmospheric pressure in Argon.

✓Residence time = 1 hour.

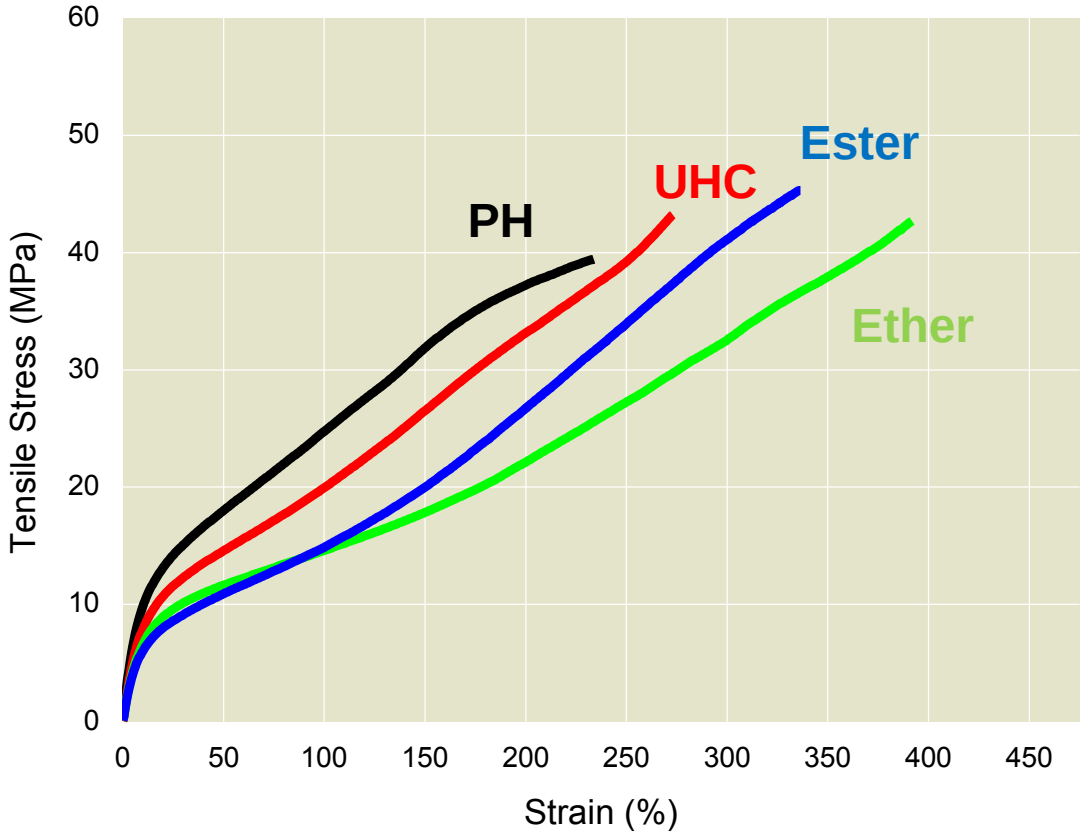
✓30 seconds at 2000 rpm after add BD

✓Curing for 12 hours at 50 bars & 100°C

Mechanical properties

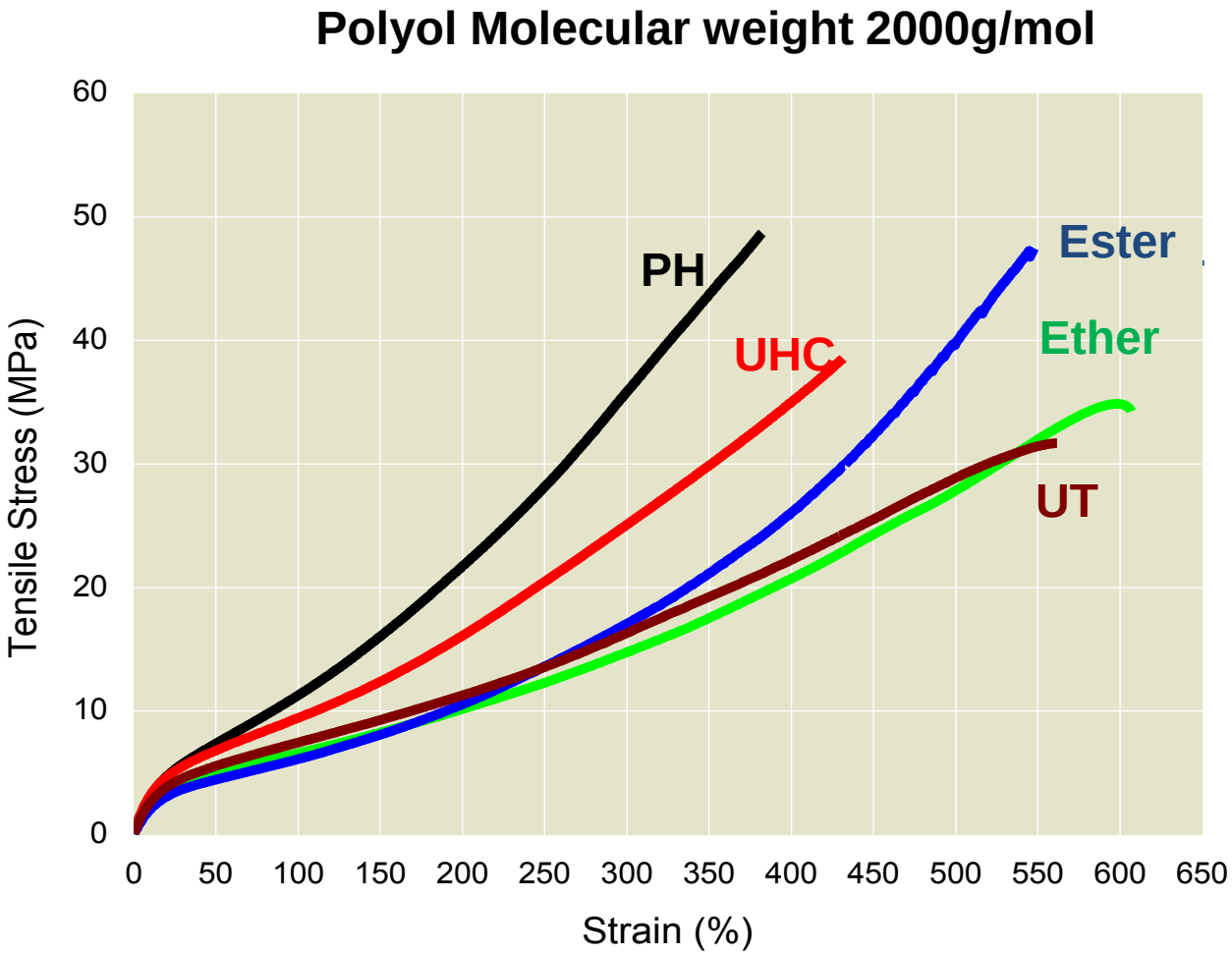
Properties	PUPH100-48	PUUHC100-48	PUPCL100-48	PUPTMG100-48
Hardness (Shore A)	92	81	--	81
Modulus elongation 100% (Mpa)	25±1	20±2	15±1	14±1
Modulus elongation 200% (MPa)	35±2	33±3	26±1	22±1
Tensile strength(Mpa)	36±3	44±4	47±2	42±3
Elongation at break (%)	235±14	256±17	361±7	382±22

Polyol Molecular weight1000g/mol

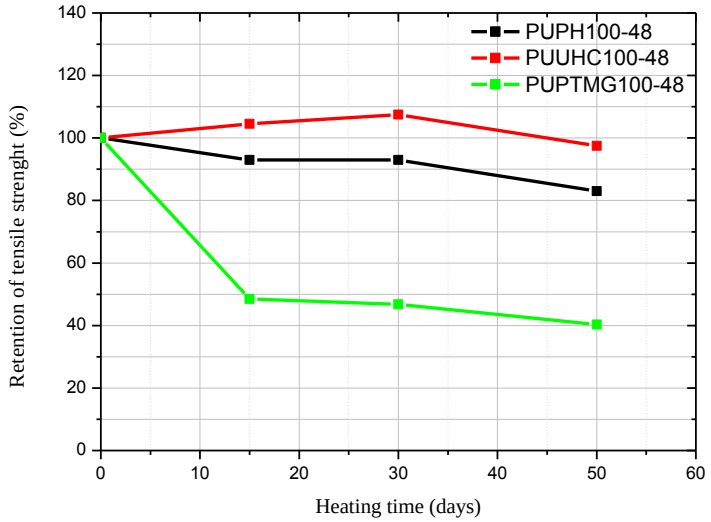


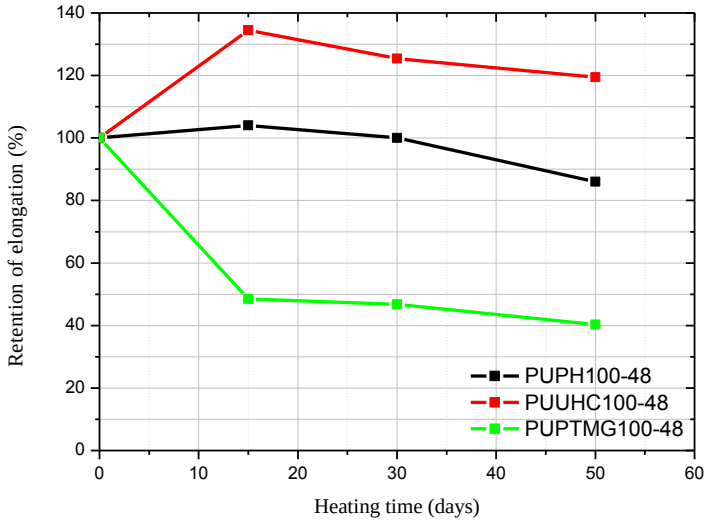
Mechanical properties

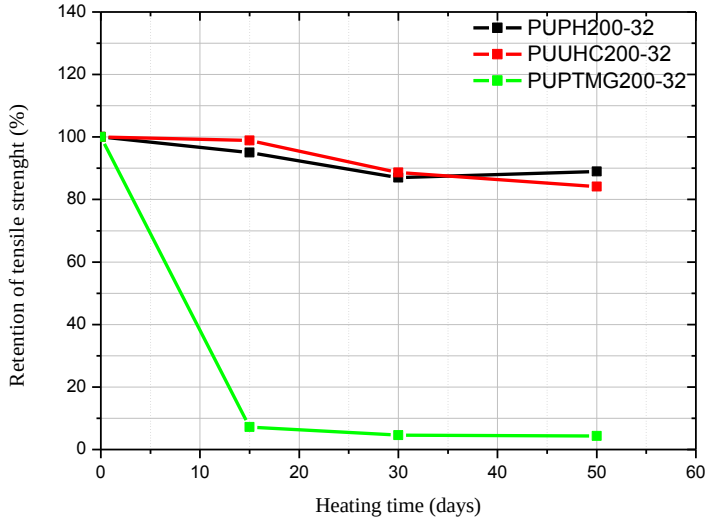
Properties	PUPH200 -32	PUUHC200 -32	PUPCL200 -32	PUUT200 -32	PUPTMG200 -32
Hardness (Shore A)	86	76	--	--	75
Modulus elongation 100% (Mpa)	12±1	8±1	6±1	8±1	7±1
Modulus elongation 200% (MPa)	24±1	14±1	10±1	11±1	11±1
Modulus elongation 300% (Mpa)	39±1	23±3	16±1	16±1	16±1
Tensile strength(Mpa)	50±2	40±6	46±5	32±1	37±4
Elongation at break (%)	358±1	458±18	560±16	557±10	610±23

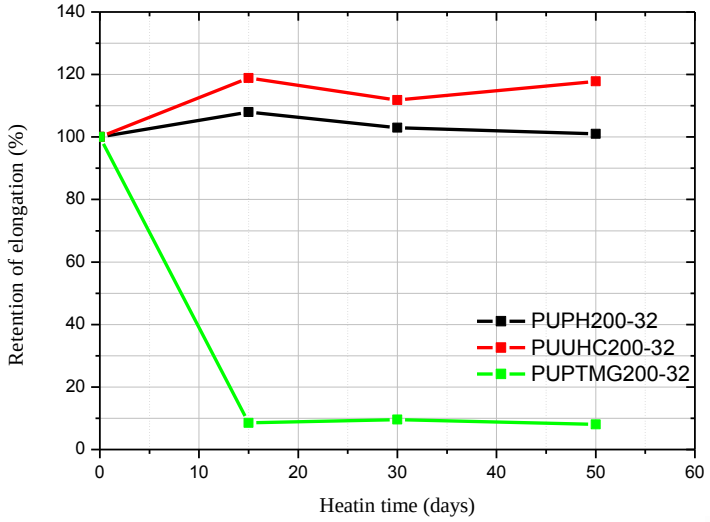


Heating resistance









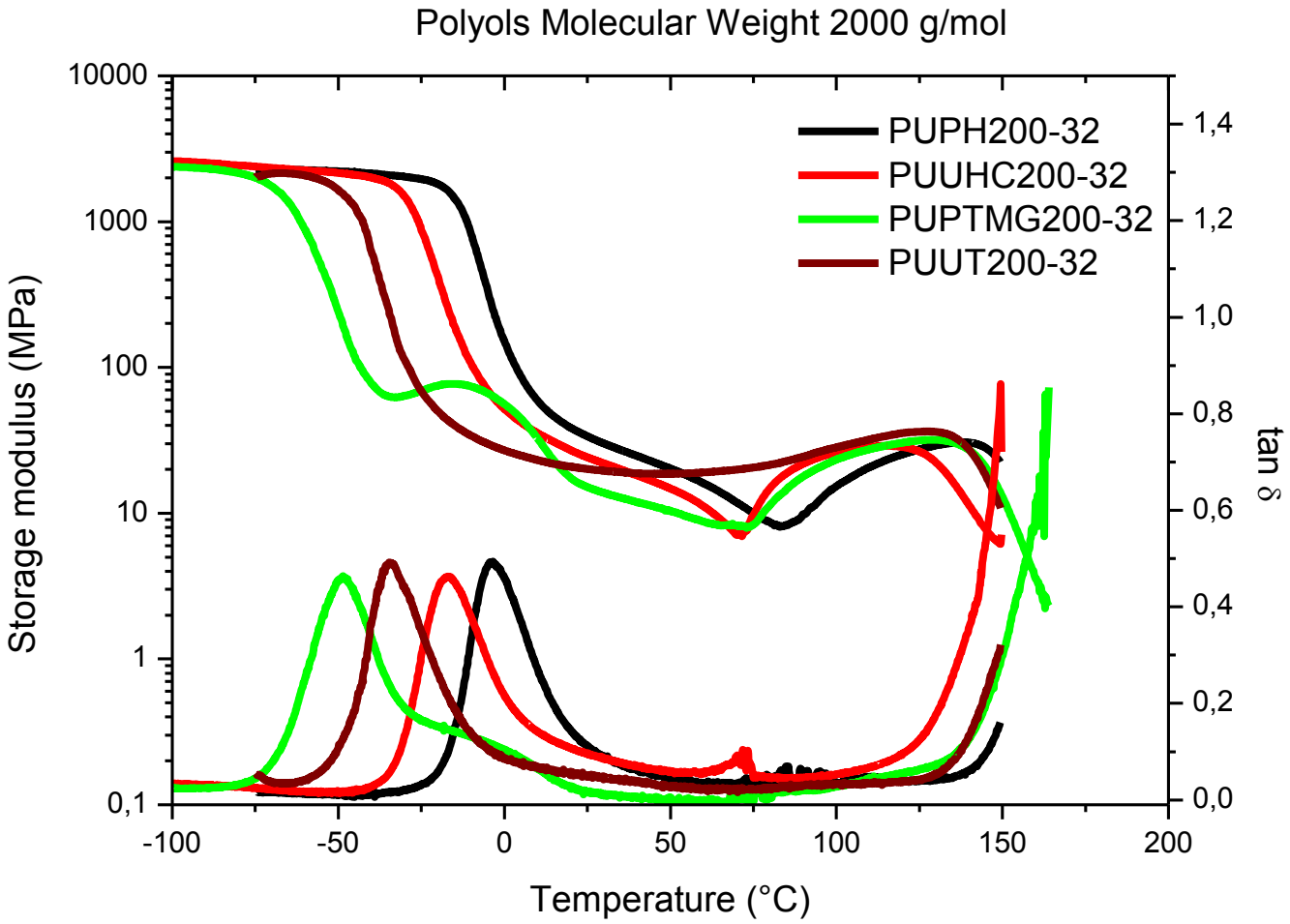


Figure Storage modulus and Tan δ as a function of temperature for the different segmented polyurethanes synthesized.

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Coatings – Properties[1]

Properties	Method	Unit	PH-100	UH-100	PPG[2]	PBA[3]
Chemical resistance	ISO 4211:1979		4	4	2	2
Hardness Persoz	ISO 1522:2007		62	121	33	109
Pencil hardness	ISO 15184:1998		3B	4B	5B	6B
Gloss 60º	ISO 2813:1999	%	99	78	79	38
Yellowness index	ASTM D1925-70		7.7	8.9	10.8	9.8
Cross-cut test	ISO 2409:2007		0	0	1	2

[1] Stainless steel plates (ISO 1514:2004), after 7 days at 23 ºC and 50%
[2] PPG: Polypropylene glycol, Mw ~ 1000
[3] PBA: Poly(1,4-butylene adipate), Mw ~ 1000

Coatings based on ETERNACOLL© show:

- Better chemical resistance
- Improved scratch resistance
- Higher gloss
- Lower yellowish
- Better adhesion to substrate

Coatings – Chemical resistance ISO 4211:1979

In a same PUD formulation, impressively noticeable results only replacing traditional polyols with **UBE ETERNACOLL®** polycarbonate diols.

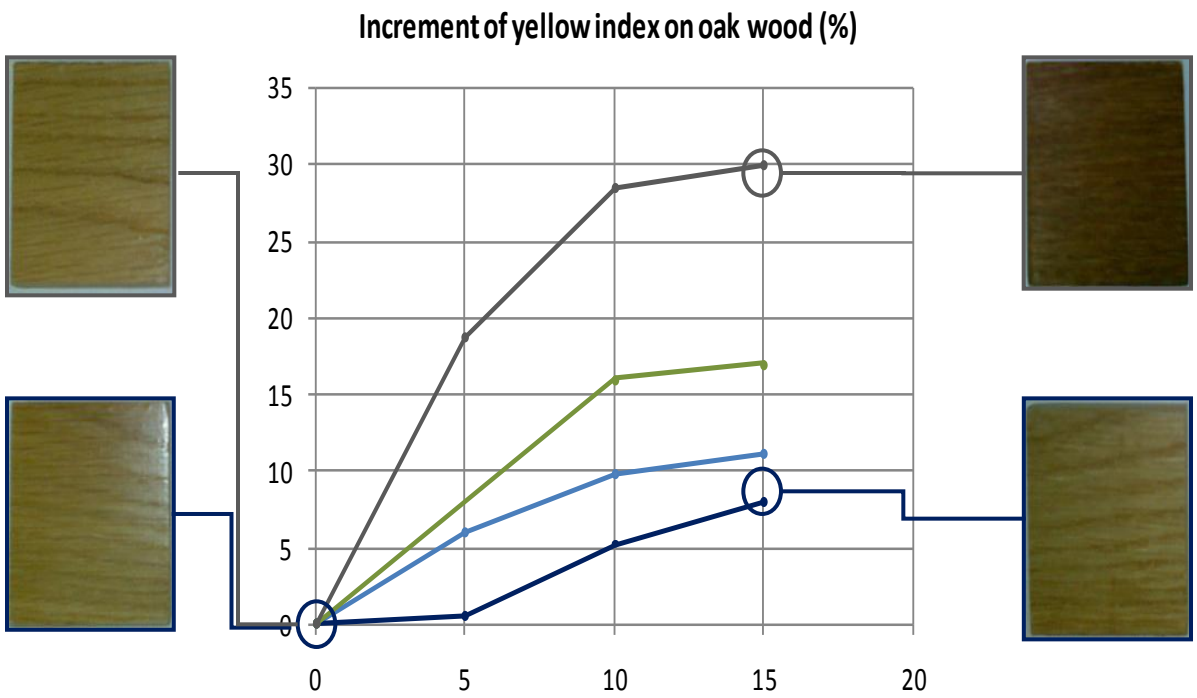
– Chemical resistance of PUD coatings just slightly depends on substrate and can be adjusted by **UBE ETERNACOLL®** polycarbonate diols molecular weight & hard segments content.

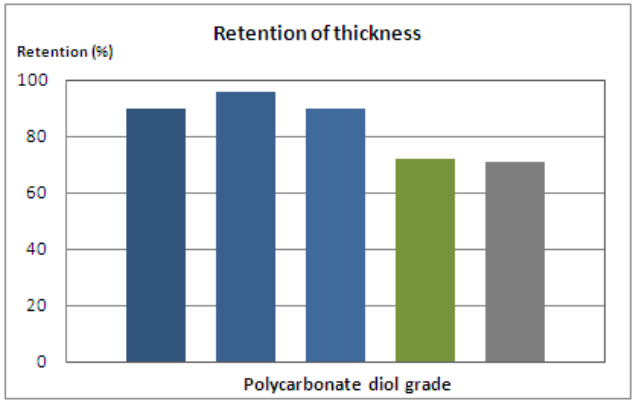
– For every substrate, there is an suitable grade of **UBE ETERNACOLL®** polycarbonate diol for providing an excellent chemical resistance to PUD coatings.

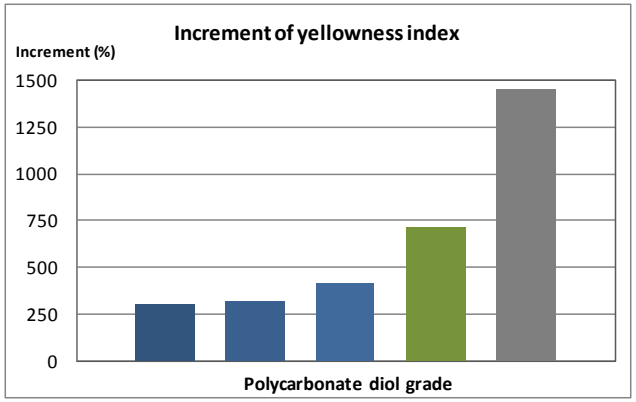
Coatings – Heat resistance

ISO 3248:1998 – Measurements after 15 days at 120 ºC

UBE ETERNACOLL® ■ BH100 ■ PH100 ■ UH100 ■ Polyether ■ Polyester

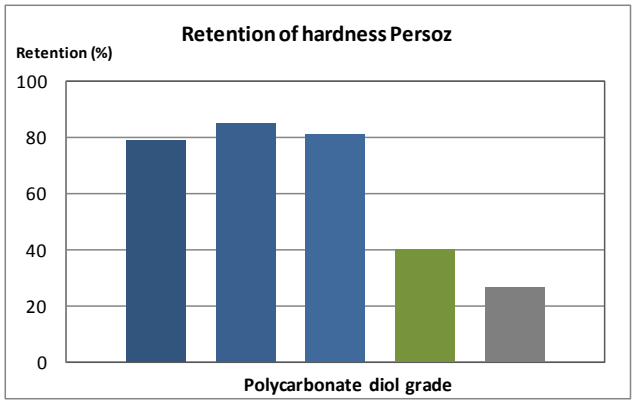


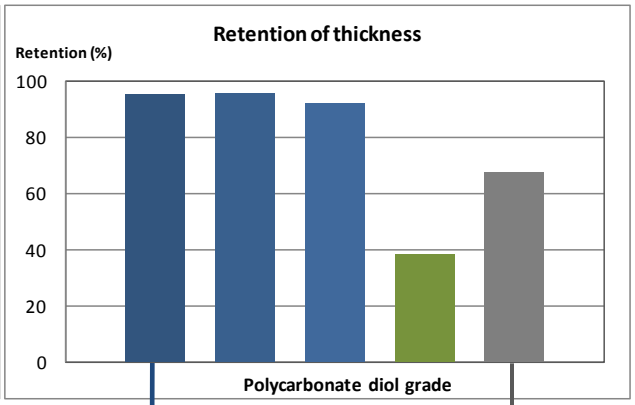


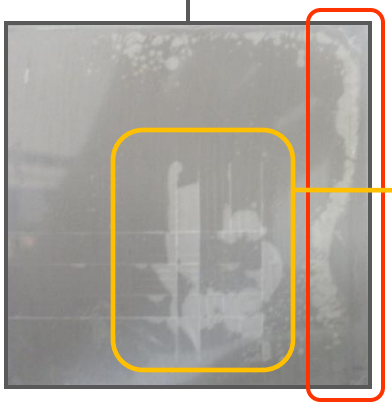


Coatings – Artificial ageing ISO 11507:2007

UBE ETERNACOLL® ■ BH100 ■ PH100 ■ UH100 ■ Polyether ■ Polyester







Worst cross cut adhesion

Loss of thickness

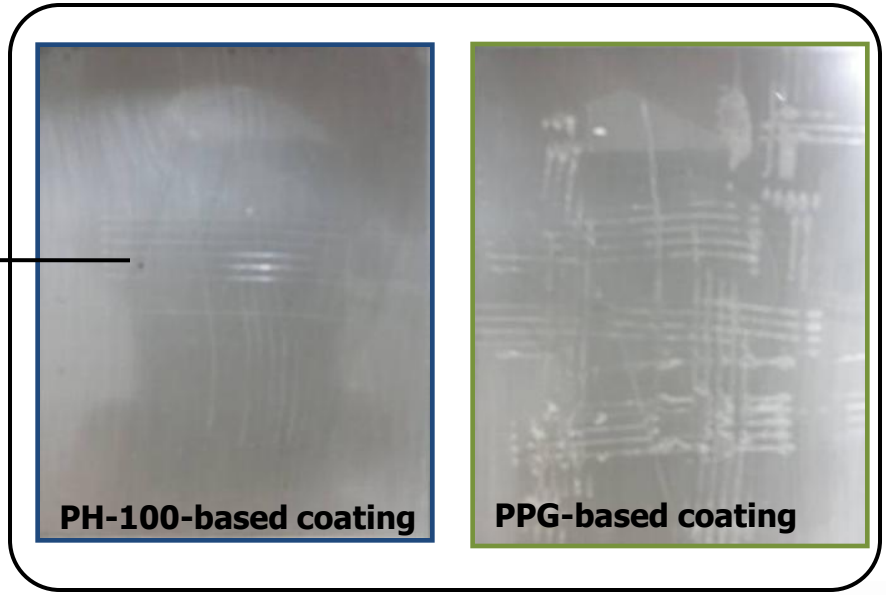
Adhesives – Properties[1]

Properties	Method	Unit	PH-100	UH-100	PPG[2]	PBA[3]
Drying time[4]	ASTM D5895-03	h	<2	<2	>6	>6
Cross-cut test	ISO 2409:2007		0	0	1	2
T-peel test	ISO 11339:2010	kN/m	1.9	2.9	0.3	1.6
Lap-shear strength	ISO 4587:2003	kPa	4.8	3.4	3.1	3.3

[1] Acetone method: % solids w/w = 38, NCO/OH in prepolymer = 1.5
Without additives
[2] PPG: Polypropylene glycol, Mw ~ 1000
[3] PBA: Poly(1,4-butylene adipate), Mw ~ 1000
[4] Dry-through time

Adhesives based on ETERNACOLL© show:

- Shorter complete drying time
- Stronger adhesion to substrates
- Improved peel resistance
- Enhanced lap-shear strength

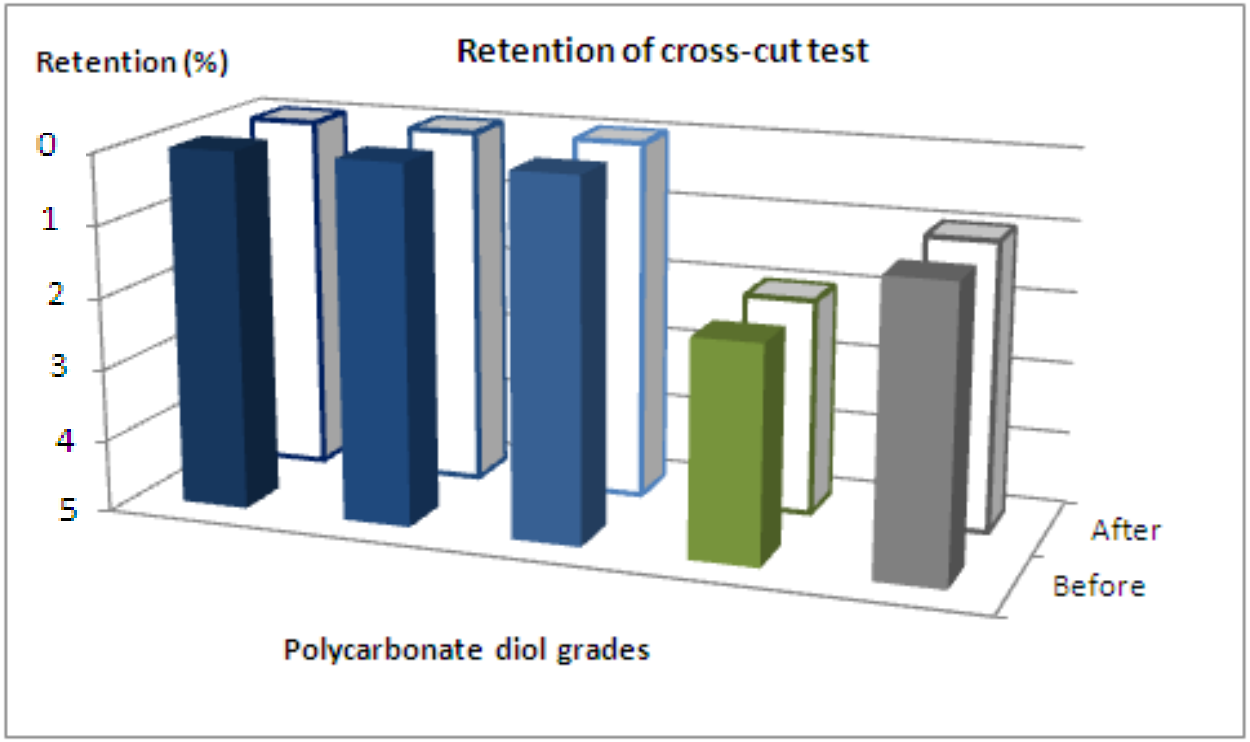


Adhesives – Heat & weather resistance

UBE ETERNACOLL® ■ BH100 ■ PH100 ■ UH100 ■ Polyether ■ Polyester

Heat resistance

ISO 3248:1998
Measurements after 15 days at 120 ºC



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Conclusions

-**PCD CAN BE USED** TO FORMULATE COATINGS, ADHESIVES AND ELASTOMERS (**CASE**)

-THE **CARBONATE** GROUP **INTERACTS MORE** THAN ESTER AND ETHER GROUP WITH HARD SEGMENT

-**CARBONATE** GROUP PROVIDE **THE STRONGEST LINKING GROUP FOR POLYOL** USED IN HIGH PERFORMANCE POLYURETANES

- **PCD ACHIEVES THE HIGHEST DURABILITY** MATERIALS AGAINST HEATING, HYDROLYSIS, CHEMICALS, WEATHERING

Applications

UBE ETERNACOLL® polycarbonate diols are recommended for PUD coatings of surfaces with chemicals and/or high heat exposure: no yellowish, excellent retention of original mechanical & adhesion properties, and gloss.

Muito Obrigado !!

Thanks for your attention !!

Further information in:
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