Polycarbonate diol
-
Improving polyurethane durability in adhesives, coatings and pavements

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Sales Executive

November 8th, 2012

OUTLINE

1. Introduction: Polycarbonate diol
2. High-performance of PUD due to polycarbonate diol: Adhesives
3. High-performance of PUD due to polycarbonate diol: Coatings
4. High-performance of polycarbonate diol-based pavements
5. Conclusions

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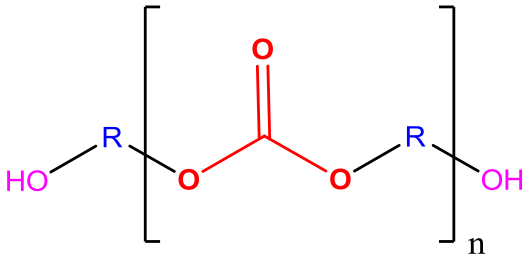
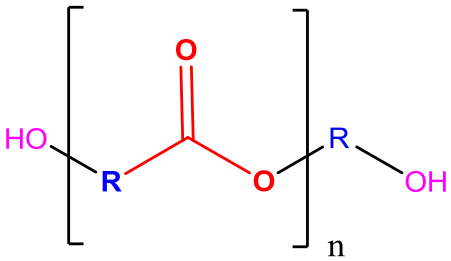
Polyols used in the synthesis of PU

Terminal – Backbone – Bridge – Backbone – Terminal



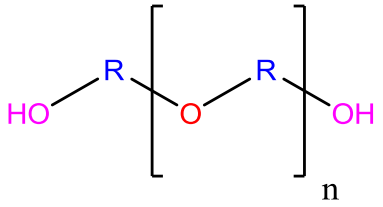
Polycarbonate diol

lower 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

Advantages provided by polycarbonate

— As PUD, Environmentally friendly

— As PUD, obey VOC regulations: Directive 2004/42/CE of the European Parliament and Council

— Similar application procedure than for traditional polyols-based polyurethane coatings and adhesives.

— Good elasticity under deformation

— Good durability and transparency

— Excellent scratch and abrasion resistance

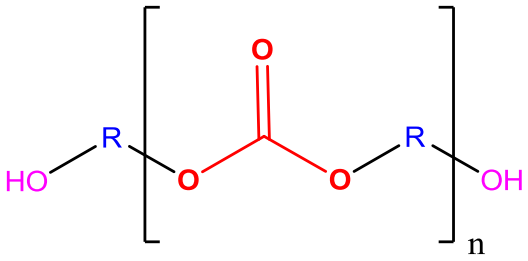
— Uniform and free of defects coatings

— Good chemical resistance

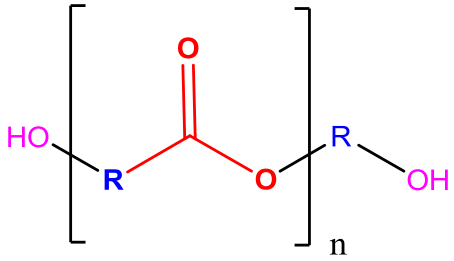
Main applications of polycarbonate diol-based PU as adhesives, coatings and pavements

Main applications of polycarbonate diol-based PU as adhesives, coatings and pavements

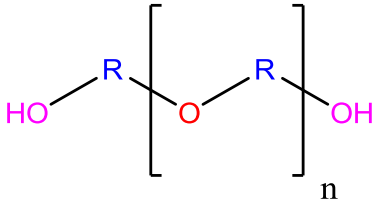
Polyols used in this work



Polycarbonate diol	Grade	R:R'	Ratio
Homopolymer	UH	1,6-hexanediol	-
Copolymer	PH	1,5-pentanediol : 1,6-hexanediol	1 : 1
Copolymer	BH	1,4-butanediol : 1,6-hexanediol	7:3 & 9:1
Copolymer	UPH	1,3-propanediol : 1,6-hexanediol	1:1
Copolymer	UM	1,4-Cyclohexanedimethanol : 1,6-hexanediol	1:3, 1:1 & 3:1
Copolymer	UHC	ε-caprolactone : 1,6-hexanediol	1:1
Copolymer	UT	Polyether : Polycarbonate	-



Polyester diol	R:R'	Ratio
1,4-butanediol adipate	1,4-butanediol : 1,6-hexanedioic acid	1:1
Polycaprolactone diol	e-caprolactone	-



Polyether diol
Polytetramethylene glycol
Polypropylene glycol

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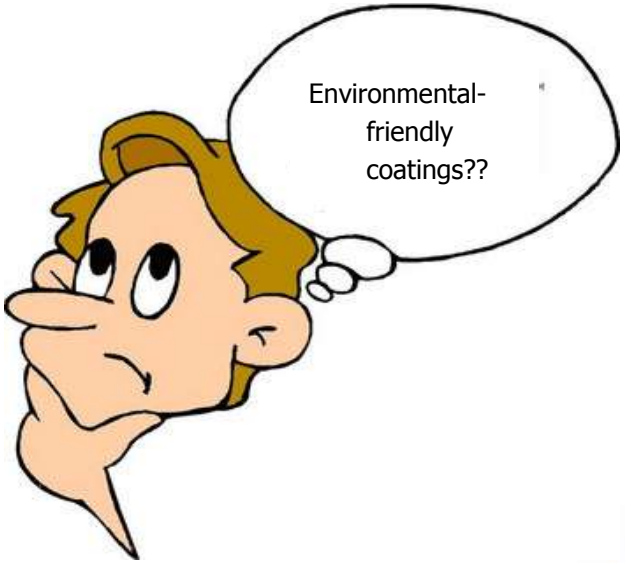
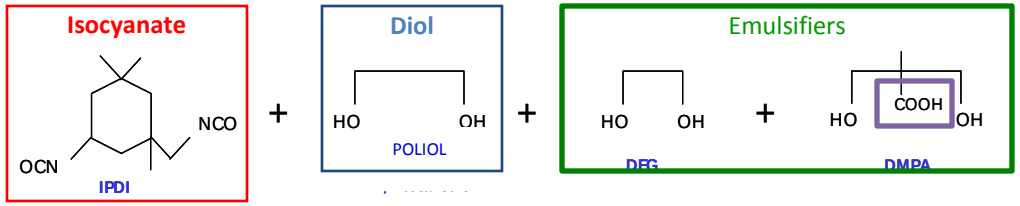
Solventborne PU solutions vs. waterborne PU dispersions

Solvent-borne coatings → VOC regulations



Waterborne polyurethane dispersions (PUDs)

Synthesis of PUD – Acetone method



1. SÍNTESIS DEL PREPOLÍMERO
T = 80°C, $V_{agitación}$ =450 rpm

PREPOLÍMERO

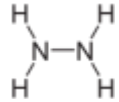
2. DISOLUCIÓN DEL PREPOLÍMERO EN ACETONA
T = 45-50°C, $V_{agitación}$ =450 rpm

3. NEUTRALIZACIÓN CON TEA
T = 45-50°C, $V_{agitación}$ =450 rpm

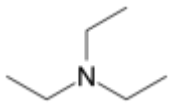
4. EXTENSIÓN DE CADENA CON HIDRACINA
T = 45-50°C, $V_{agitación}$ =450 rpm

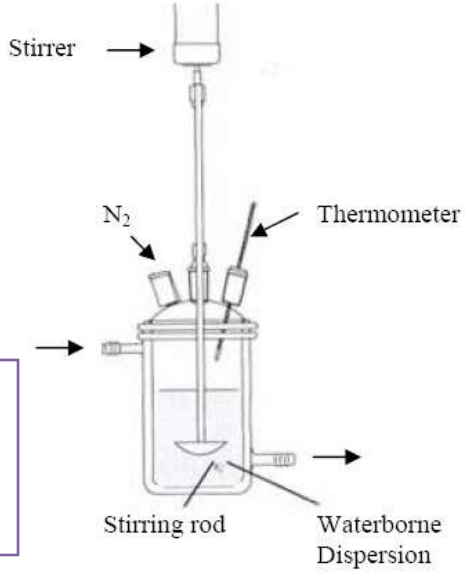
5. ADICIÓN DE AGUA
T = 45-50°C, $V_{agitación}$ =900 rpm

Chain extender



Neutralizer



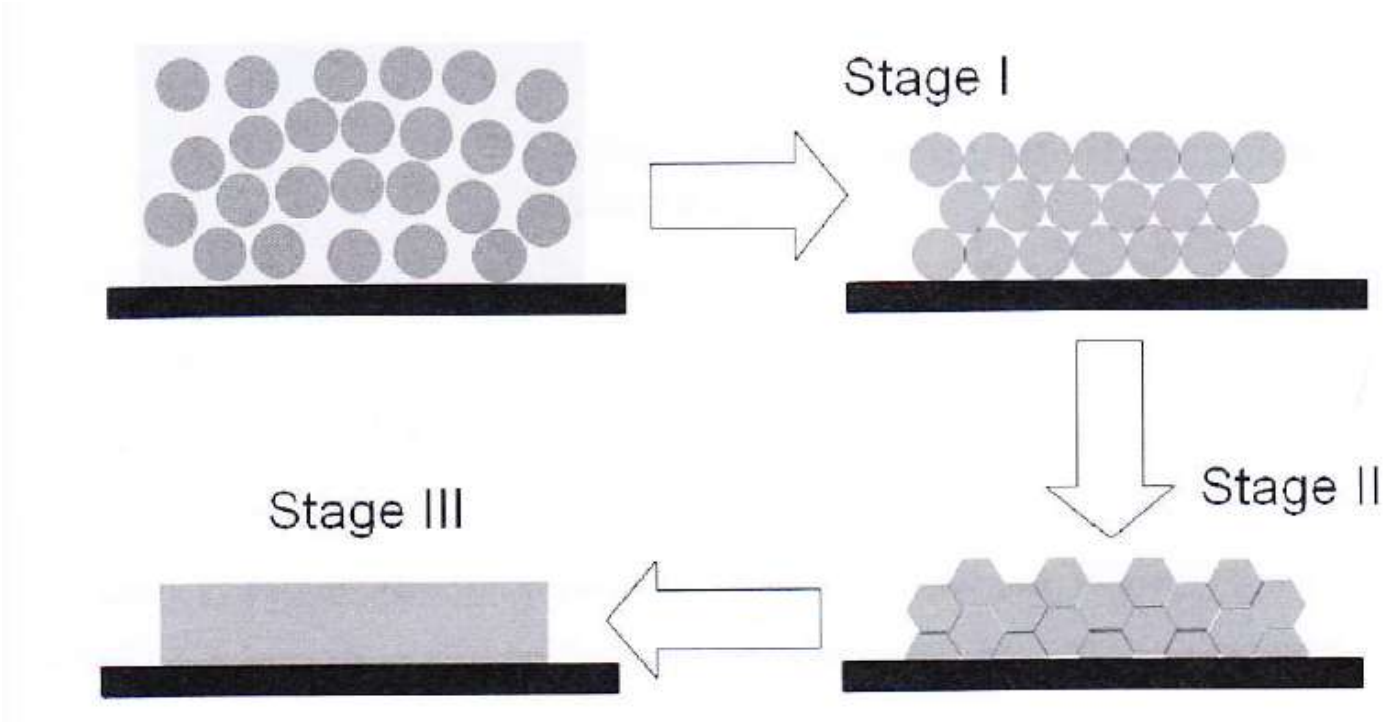


DISPERSIÓN DE POLIURETANO EN AGUA/ACETONA

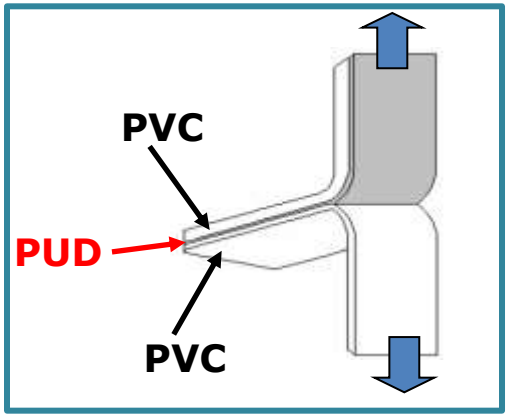
6. DESTILACIÓN DE LA ACETONA
T = 50°C, P = 300mbar

DISPERSIÓN ACUOSA DE POLIURETANO

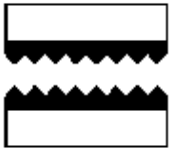
Waterborne PU dispersions: Curing process



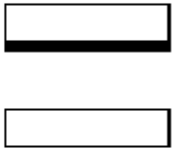
Adhesives – T-peel test



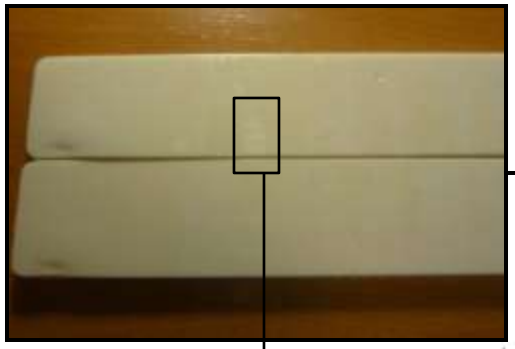
CA: Cohesive failure in the adhesive



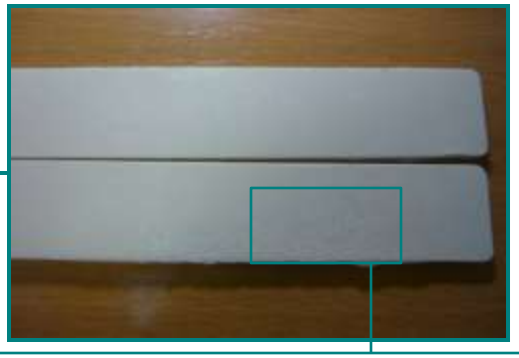
A: Adhesion failure



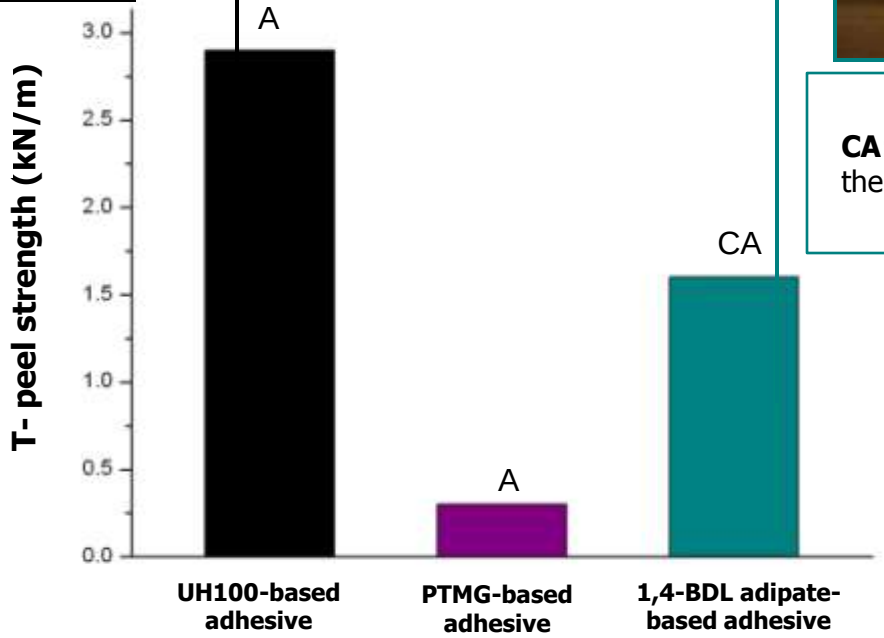
Adhesives – T-peel test Comparative Polycarbonate/Polyether/Polyether



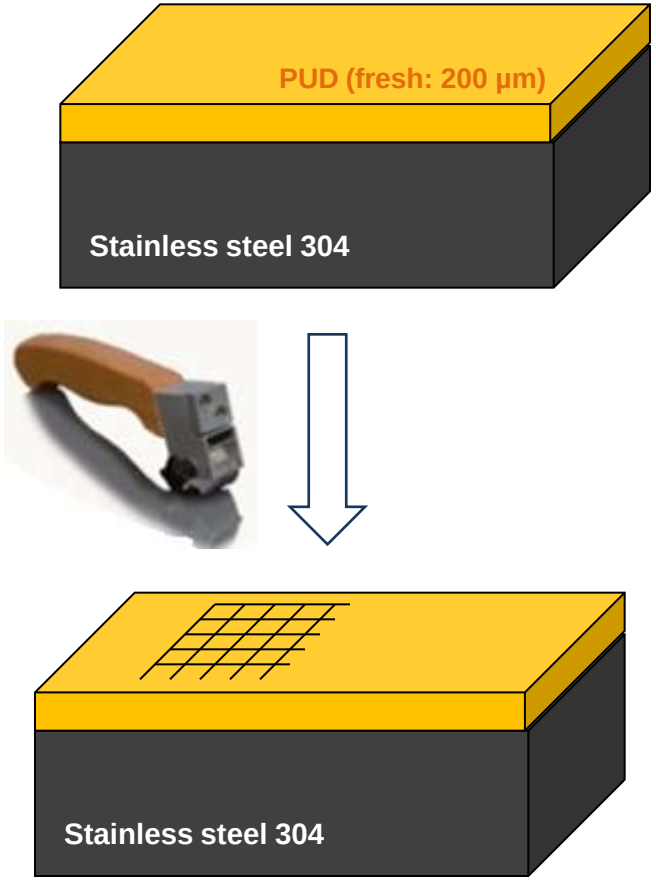
A: Adhesion failure

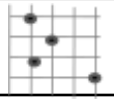
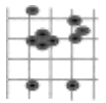
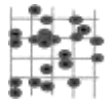
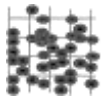


CA: Cohesive failure in the adhesive



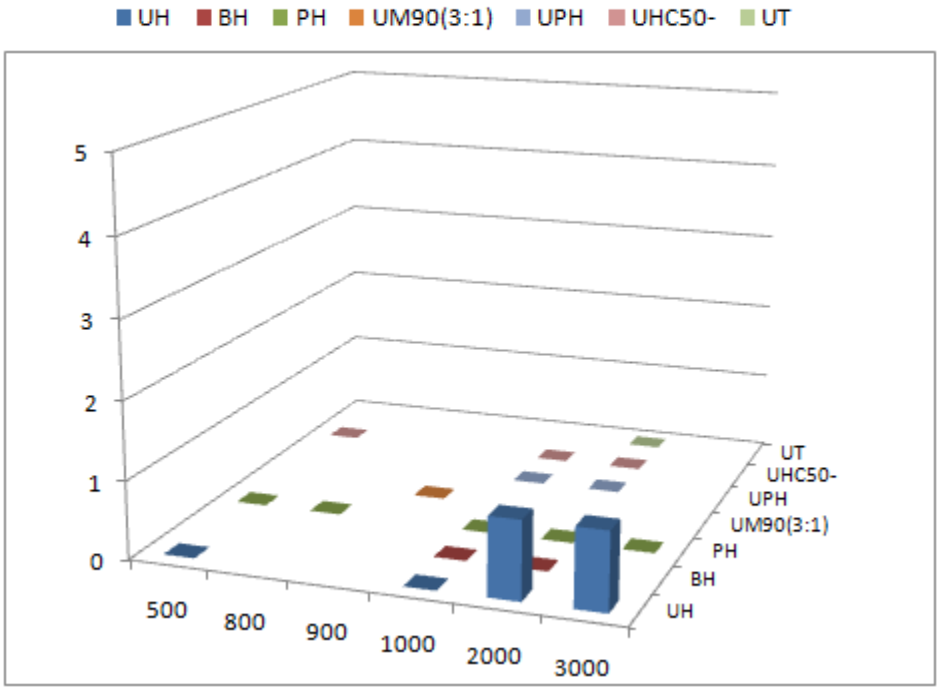
Adhesives – Ageing, as variation of cross-cutter adhesion test



Code	Description	Damaged surface
0	No modification	-
1	Light loosening of coating (< 5 %)	
2	Light loosening of the borders of the coating (5 to 10 %)	
3	Partial loosening of the coating (15 to 35 %)	
4	Strong loosening of the coating (35 to 65 %)	
5	Very strong loosening of the coating (> 65 %)	

Adhesives – Ageing, as variation of cross-cutter adhesion test

Grade	As dispersion		As coating
	T-peel (kN/m)	Lap shear (kPa)	Cross-cutter adhesion
UH50	0,2	3,1	0
UH100	2,9	3,4	0
UH200	2,1	2,9	1
UH300	1,1	1,7	1
BH100	0,2	4,9	0
BH200 (9.1)	0,6	3,6	0
BH200 (7.3)	2,0	5,8	0
PH50	0,2	6,0	0
PH80D	1.2	4,0	0
PH100	1,9	4,8	0
PH200D	1,7	1,9	0
PH300D	3,2	3	0
UM90 (1.3)	1,1	6,6	0
UM90 (1.1)	0,7	8,0	1
UM90 (3.1)	0,6	7,2	---
UPH100	0,4	6,0	0
UPH200	0,9	4,6	0
UHC50-50	0,8	7,0	0
UHC50-100	4,0	6,1	0
UHC50-200	2,8	4,3	0
UT200	2.7	3	0



Trends:

i. Molecular weight:

No dependence, but UH200 & UH300

ii. Homopolymer vs. copolymer:

No dependence

Adhesives – Ageing, as variation of cross-cutter adhesion test

Polycarbonate diol PUD - based

No modification

Polypropylene Glycol PUD - based

Light loosening of the borders of the coating

Polycaprolactone PUD - based

Loosening of the coating

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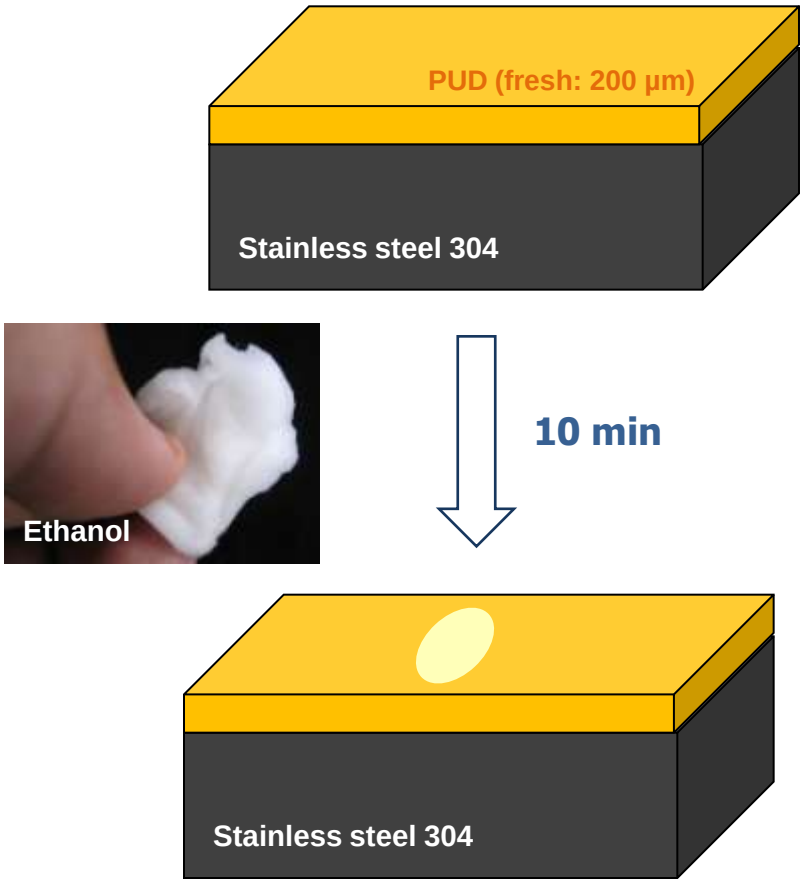
Coatings – Chemical resistance



Code	Damaged Surface
5	Intact coating
4	Slight change in gloss or color
3	Light mark
2	Strong mark
1	Coating removal

Coatings – Chemical resistance of coatings based on Polycarbonatediol vs. polyester diol vs. polyether diol

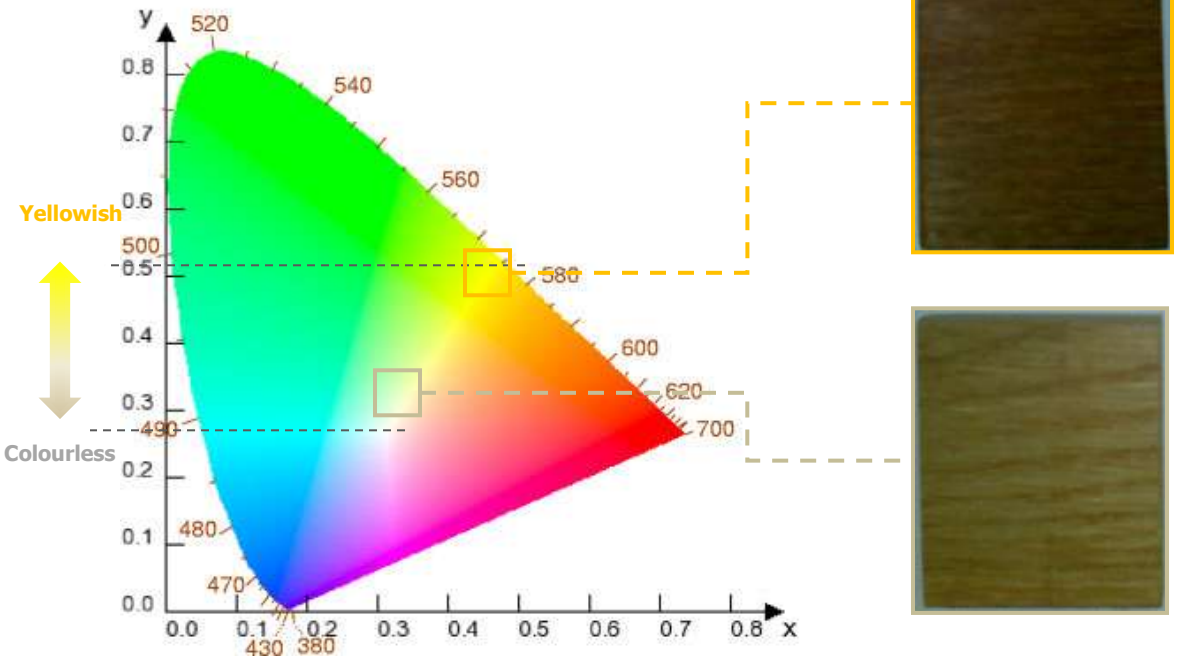
PTMG-based PUD

1,4-BDL adipate-based PUD

UH100-based PUD

Code	Damaged Surface
5	Intact coating
4	Slight change in gloss or color
3	Light mark
2	Strong mark
1	Coating removal

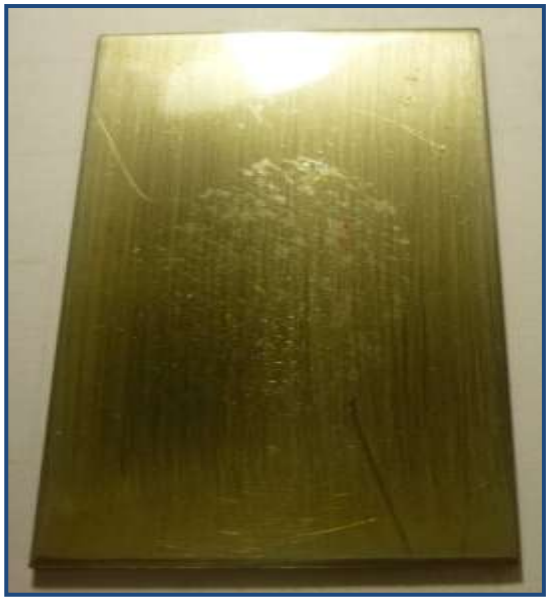
Coatings – Yellowness index



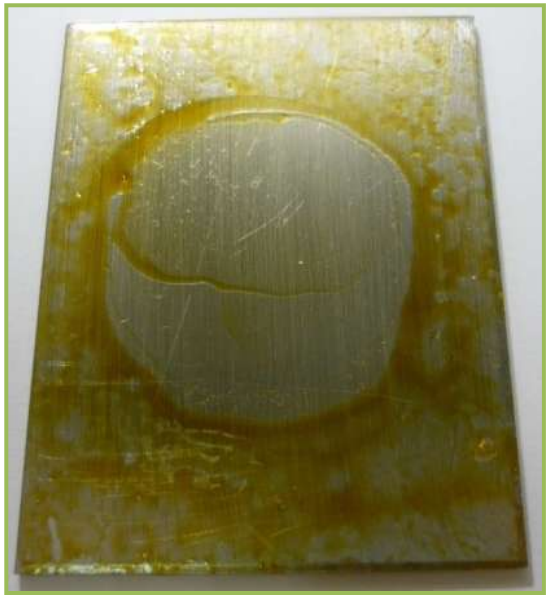
CIE 1931 color space chromaticity diagram

Coatings – Ageing, as increment of yellowness index and retention of thickness

Heat resistance: ISO 3248:1998 (15 days @ 120 ºC)



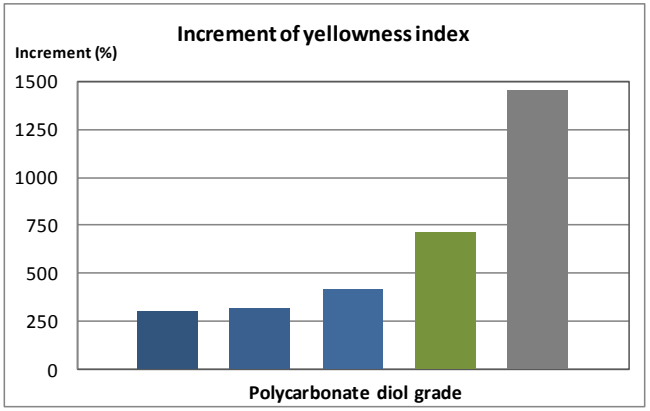
UH100-based PUD

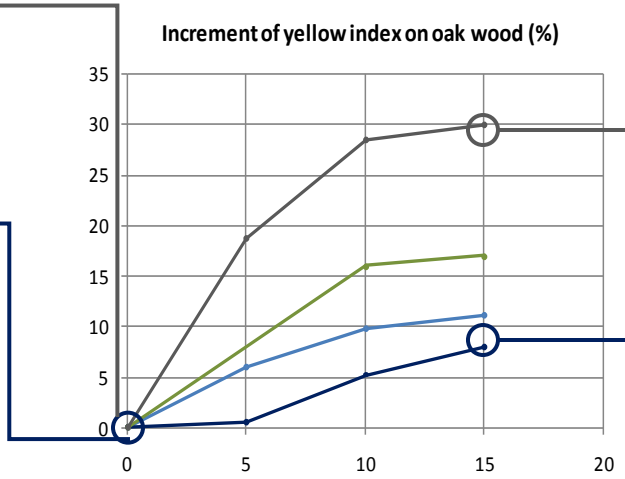


PPG-based PUD

1,4-BDL adipate-based PUD

Coatings – Ageing, as increment of yellowness index





Coatings – Ageing, as retention of thickness

Artificial weathering: ISO 11507:4892-3 (Cycle H)

UH100-based PUD

Blistering

PPG-based PUD

Loss of thickness

1,4-BDL adipate-based PUD

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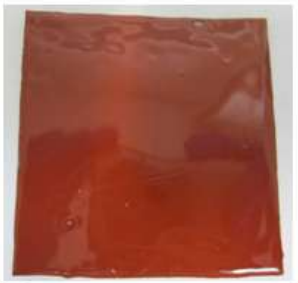
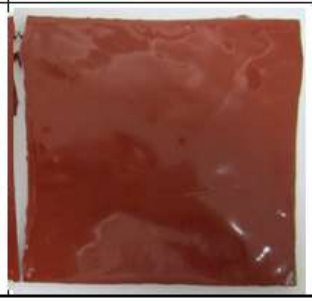
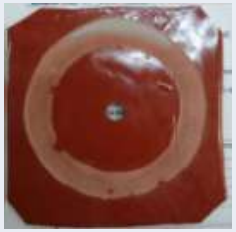
Pavement – Chemical resistance

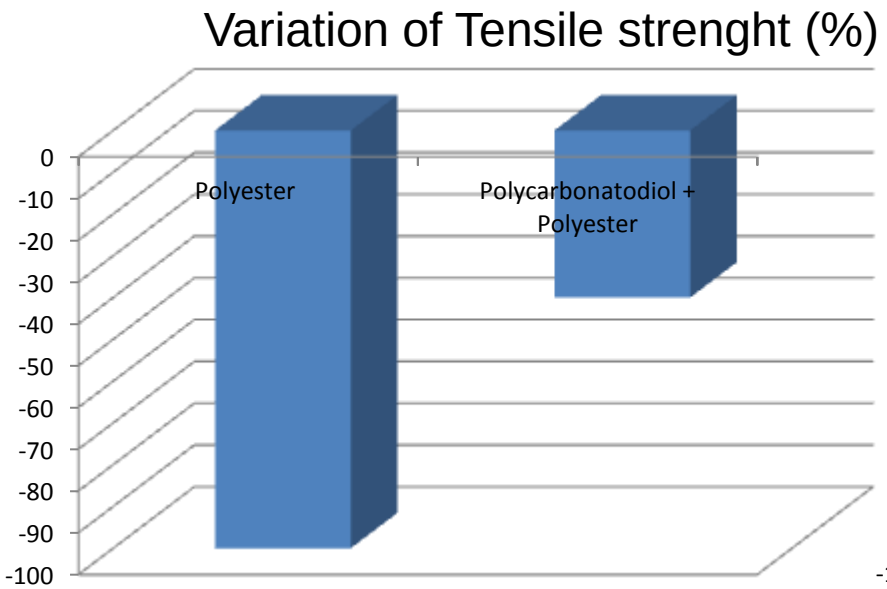
	Without treatment	Ethanol	Motor oil	Gasoline	Brake fluid
Polyester based pavement					
50% Polycarbonate diol + 50% Polyester based pavement					

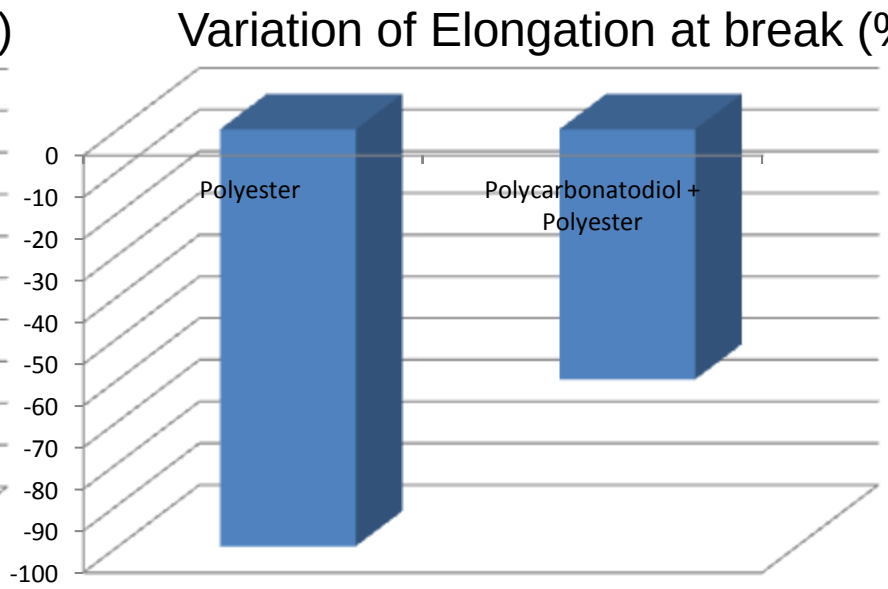
Test conditions: Direct contact, 24h @ 23 ºC, 50% R.H.

Pavement – Improvement of mechanical properties

Pavement	Pencil hardness (ISO 15184)	Persoz hardness (ISO 1522)	Abrasion resistance (lost mg / 100 cycles, ISO 5470)
Polyester	6B	19	32 
Polycarbonate diol-based	4B	36	12 

Pavement – Hydrolysis resistance





Test conditions: Water immersion, 80ºC for 32 days; ISO527

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Using polycarbonate diol, we can conclude about durability that …

Adhesives based on polycarbonate diol show:

- Enhanced retention of initial adhesion properties after ageing
- No losses of adhesion

Adhesives

Coatings based on polycarbonate diol show:

- Better retention of initial mechanical properties after ageing
- Lower yellowness increment
- Less thickness losses
- Minor blistering

Coatings

Pavements including polycarbonate diol show:

- Improved resistance to automotive chemicals
- Enhanced abrasion resistance
- Better retention of initial mechanical properties after hydrolytic ageing

Pavements

Acknowledgments

University of Alicante
ADHESION AND ADHESIVES

Laboratory of Adhesion and Adhesives (University of Alicante, Spain) for synthesis and experimental characterization of the PUDs and polyurethane adhesives.

UBE Corporation Europe S.A.

Thanks for your attention !!

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