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

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INTRODUCTION

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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.

Fillers and additives have been used to improve abrasion resistance of polyether and polyester-based polyurethane coatings


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.

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
Automotive finishing

Artificial leather

Leather finishing

Automotive finishing

Flooring

Wood coating & paints
Adhesives

Bioadhesives

TPU & elastomers

Rollers

Footwear

RIM foams
Inks

Oil & mining

Encapsulation

Pavements

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
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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


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

![Graph depicting NCO/OH weight percentage vs. polycarbonate diol weight percentage. The graph shows data points for various concentrations of polycarbonate diol, with corresponding NCO/OH ratios.]
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<table>
<thead>
<tr>
<th>Formulation</th>
<th>Pot life (min)</th>
<th>Viscosity (mPa·s)</th>
<th>Abrasion resistance (mm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specification</td>
<td>10-16</td>
<td>&lt; 2000</td>
<td>&lt; 50 mm</td>
</tr>
<tr>
<td>Polycarbonate diol-free blank</td>
<td>on spec</td>
<td>on spec</td>
<td>34</td>
</tr>
<tr>
<td>PH50-including optimization</td>
<td>13.5</td>
<td>870</td>
<td>4</td>
</tr>
</tbody>
</table>

- 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
NCO/OH  vs  polycarbonate diol (wt%)  

HARDNESS

OPTIMAL REGION
Abrasion resistance (mg) vs. PH50 (wt%). PH50 > 50wt% indicates an optimal region.
Before abrasion

100wt% PTMG

50wt% PTMG + 50wt% polycarbonate diol

100wt% polycarbonate diol

After abrasion

500 μm

500 μm

500 μm
Before ageing

100 wt% PTMG

60 wt% PH50 + 40 wt% PTMG

After ageing
PU – 60wt% PH50+ 40wt% PTMG

PU – 100wt% PTMG

Stress $\sigma$ (MPa)

Strain $\varepsilon$ (%)
Tear strength (kN/m)

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)
### Variation (%)

<table>
<thead>
<tr>
<th>Property</th>
<th>100wt% PTMG</th>
<th>60wt% PH50 + 40wt% PTMG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic modulus</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength</td>
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<tr>
<td>Yield point</td>
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<td></td>
</tr>
<tr>
<td>Break strength</td>
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<tr>
<td>Elongation at break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resilience</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toughness</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Legend:**
- Red: 100wt% PTMG
- Blue: 60wt% PH50 + 40wt% PTMG
<table>
<thead>
<tr>
<th>Polyurethane composition</th>
<th>Before ageing</th>
<th>After ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>100wt% PTMG</td>
<td>-57%</td>
<td>-43%</td>
</tr>
<tr>
<td>60wt% PCD + 40wt% PTMG</td>
<td>-43%</td>
<td>-43%</td>
</tr>
</tbody>
</table>
Introduction

Experimenta

Results and discussion

Conclusions
- 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
✓ Envie um e-mail a d.Hernandes@ube.ind.br
✓ Fale com Daniel Hernandes – 11 9 6640 6053