

**OXYMER® - A NEW CLASS OF POLYCARBONATE MACRODIOLS FOR
WATERBORNE COATINGS WITH EXCELLENT PERFORMANCE**

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ABSTRACT

A new class of versatile aliphatic polycarbonate macrodiols has been developed by Perstorp. In this paper these polycarbonates are evaluated and compared to other types of conventional macrodiols in aqueous polyurethane dispersions. This new class of polycarbonate macrodiols includes homo- or co-polymers derived from 2,2-dialkyl-1,3-propanediols. From the aqueous anionic polyurethane dispersions polymer films were cast and evaluated according to several different coating evaluation methods such as hardness, flexibility, chemical, abrasion and outdoor resistance. These newly developed polycarbonates all show a high hardness, very good adhesion, excellent water, acid and base resistance and very good weathering resistance.

Introduction

Aqueous polyurethanes have proved to become versatile products for a wide variety of applications both in coatings and adhesives. Polyurethane dispersions (PUD's) are flexible and tough, and can be formulated to fit a wide range of applications. They form a respected and appreciated class of high performance, high value added coating materials. Polyurethane dispersions can be formulated for a range of different properties suitable for a number of different applications and for the whole range of elasticity requirements. The properties of the PUD's can be formulated as very soft and flexible, suitable for e.g. textile and leather, as moderately elastic for products like wood and plastics or at the other extreme, as hard coatings for metals and mineral surfaces. Many polyurethane coating formulators often seek a combination of elasticity, even at low temperatures, outdoor durability, chemical resistance and hydrolytic stability to obtain a long-lasting product. The combination of elasticity and hydrolytic stability within a polyurethane formulation is often achieved with a polyether polyol. However, polyethers are known to be sensitive to auto-oxidation and have poor outdoor durability. Chemical resistance and outdoor durability can be obtained using a polyester polyol, but in that case the requirements for hydrolytic stability of the polyurethane are more difficult to fulfil since polyesters are known to be sensitive to degradation in both acidic as well as alkaline media. In addition polyesters are often relatively hydrophilic, which facilitates the dissolution and diffusion of acids and bases.

Combining hydrolytic and outdoor stability in a coating, while maintaining good adhesion, flexibility and abrasion resistance is often problematic. The use of aliphatic polycarbonates in polyurethane dispersions could offer a solution to this obstacle. Today the polycarbonate used universally is 1,6-hexanediol based. To broaden the available range of polycarbonate diols and increase their use in coating applications a new class of polycarbonate diols derived from 2,2-dialkyl-1,3-propanediols has been developed. This new class of polycarbonate diols are named Oxymer®.

Contrary to the traditional hexanediol polycarbonate the newly developed polycarbonates contain substituted aliphatic diols which offer new unique properties and hence new formulation possibilities. This new class of polycarbonate macrodiols includes homo- and co-polymers derived from Perstorp polyols, e.g. the BEPD (butyl-ethyl propane diol) polycarbonate, Oxymer M, which is an amorphous liquid hydrophobic polycarbonate diol suitable for low surface energy, hard and resistant coatings. The high hydrophobicity of this polycarbonate offers advantages such as very good wetting properties, improved weathering resistance and chemical resistance. The co-polymer polycarbonate, Oxymer C, is also liquid and amorphous and displays similar properties to the BEPD polycarbonate, such as improved chemical resistance as well as high hardness and flexibility.

In this paper the evaluation of these aliphatic polycarbonate diols in anionic aqueous polyurethane dispersions, including coatings prepared thereof, is reported. Together with the polycarbonates different commercial macrodiols, i.e. a polyester, polyether, polycaprolactone, as well as the commonly used polycarbonate based on 1,6-hexanediol, have been included. The benefit of utilizing the Oxymer polycarbonates compared to the other macrodiols is demonstrated with respect to hardness, chemical resistance and outdoor durability, for example.

Experimental

Aqueous anionic polyurethane dispersions were prepared from the macrodiols listed in Table 1 and Table 2, isophorone diisocyanate (IPDI) and α,α -dimethylol propionic acid (Bis-MPA) in 1-Methyl-2-pyrrolidinone (NMP) using the prepolymer mixing process in a five necked glass reactor equipped with a thermometer, anchor stirrer, condenser and nitrogen inlet. Macrodiols with a molecular weight of 1000 g/mol and 2000 g/mol were utilized. When a constant NCO value was obtained, as determined by the NCO standard back titration method, the carboxylic acid groups in the prepolymer were neutralized by the addition of triethyl amine (TEA) to render them water dispersible. The NCO terminated polymer chains were then dispersed in water and chain extended with 1,2-ethylene diamine (EDA). See Table 3 together with Table 4 for the composition and data of the prepared PUDs.

The final polyurethane dispersions were characterised with respect to pH and viscosity, see Table 5 (1000 g/mol macrodiols) and Table 6 (2000 g/mol macrodiols).

The PUD's were applied to glass, black glass and aluminium substrates using a 100 μm K-wire bar applicator. The samples were force dried at 80 °C for 24 h, then left at 23 °C and 50 percent relative humidity for another 24 h before coating evaluation.

Table 1. The macrodiols (molecular weight of approximately 1000 g/mol) used in the different aqueous anionic polyurethane dispersions, their viscosity and glass transition temperature

| Macrodiol 1000g/mol | OH number (mg KOH/g) | Viscosity @ 75 °C (Pas) | T_g/T_m (°C) |
|-------------------------------|-------------------------|----------------------------|-------------------|
| Oxymer M112 | 112 | 1.1 | -23/- |
| Oxymer C112 | 109 | 1.6 | -33/- |
| HD polycarbonate ¹ | 112 | 0.4 | -61/45 |
| Polyester ² | 112 | 0.4 | -55/- |
| Polyether ³ | 112 | 0.1 | -/31 |
| Polycaprolactone ⁴ | 112 | 0.1 | -/34 |

¹. Hexane diol polycarbonate

². Neopentylglycol-adipic acid

³. Poly(tetramethylene ether) glycol

⁴. Neopentylglycol initiated polycaprolactone

Table 2. The macrodiols (molecular weight of approximately 2000 g/mol) used in the different aqueous anionic polyurethane dispersions, their viscosity and glass transition temperature

| Macrodiol 2000g/mol | OH number (mg KOH/g) | Viscosity @ 75 °C (Pas) | T_g/T_m (°C) |
|-------------------------------|-------------------------|----------------------------|---------------------|
| Oxymer M56 | 60 | 2.0 | -21/- |
| Oxymer C56 | 55 | 8.3 | -27/- |
| HD polycarbonate ¹ | 62 | 2.0 | ND ² /51 |

¹. Hexane diol polycarbonate

². Not detectable

Table 3. Composition of the PUD's. The quantities of dispersing agent and diisocyanate were adjusted with respect to the OH number of the macrodiol

| General PUD formulation | 1000 g/mol | 2000 g/mol |
|-------------------------|------------|------------|
| Macrodiol | 16.7 | 19.5 |
| Bis-MPA | 2.2 | 2.1 |
| IPDI | 10.4 | 7.9 |
| NMP | 10.0 | 10.0 |
| DBTL | 0.005 | 0.005 |
| Triethyl amine (TEA) | 1.4 | 1.4 |
| Water | 58.6 | 58.6 |
| Ethylene diamine | 0.6 | 0.5 |
| Total: | 100.0 | 100.0 |

Table 4. Theoretical data of the synthesized PUD's.

| Theoretical data | 1000 g/mol | 2000 g/mol |
|-------------------------------|------------|------------|
| Bis-MPA/macrodiol molar ratio | 1.0 | 1.6 |
| NCO/OH ratio | 1.4 | 1.4 |
| NH/NCO ratio | 0.8 | 0.8 |
| TEA/COOH ratio | 0.85 | 0.85 |
| Non volatile content, % m/m | 30 | 30 |

Table 5. Viscosity and pH of the different polyurethane dispersions (1000 g/mol macrodiols)

| Macrodiol | Viscosity @23 °C ¹ | pH |
|------------------|-------------------------------|-----|
| Oxymer M112 | 125 | 8.0 |
| Oxymer C112 | 38 | 9.6 |
| HD polycarbonate | 34 | 9.2 |
| Polyester | 45 | 8.7 |
| Polyether | 63 | 8.3 |
| Polycaprolactone | 42 | 8.0 |

¹. Brookfield DV-II+, 20 rpm

Table 6. Viscosity and pH of the different polyurethane dispersions (2000 g/mol macrodiols)

| Macrodiol | Viscosity @23 °C | pH |
|------------------|------------------|-----|
| Oxymer M56 | 28 | 8.0 |
| Oxymer C56 | 26 | 9.1 |
| HD polycarbonate | 90 | 9.7 |

Differential Scanning Calorimetry was performed using a Mettler DSC 30LN. The glass transition- and melting temperatures were determined during the second heating scan at a heating rate of 10 °C/min after a cooling scan from 80 °C to -100 °C at a cooling rate of 10 °C/min. Glass transition temperatures were in the case of some semi-crystalline macrodiols not possible to detect.

The hardness was evaluated using a pendulum hardness tester (according to DIN EN ISO 1552) and pencil hardness tester (according to ISO 15184). The flexibility was determined with an Erichsen testing equipment (according to ISO 1520) and the chemical resistance by chemical spot tests (according to ISO 4211).

The abrasion resistance of the PUD's was estimated with the so-called Scotch Brite™ gloss retention test. The initial gloss of the coating which had been applied to a black glass panel was measured at an angle of 85°, the surface was then rubbed with a Scotch Brite™ sponge at a load of 385 g and the gloss was measured after 10 and 50 double rubs. In this test the gloss retention is an estimate of the abrasion resistance where high gloss retention is an indication of a higher abrasion resistance.

The adhesion was evaluated as the amount of material still adhering to the substrate after being subjected to a cross cut using a 5 tapered teeth cross cut tester with 1 mm spacing. The result was graded on a scale of 0 to 5, where 0 equals no loss of material and 5 equals a complete loss of all the coating material within the tested area.

In the spot test method a cotton pad soaked in the liquid to be tested was placed on the coating and covered by a cup for the desired exposure time. After the test, the cup and cotton pad was removed and the surface gently wiped with a paper tissue and left to recover for 24 h in a constant climate chamber before evaluation. The result was graded on a scale of 1 to 5, where 5 equals no visible change in the coating surface and 1 equals a distinct mark with an altered surface.

The contact angle of water drops on cured coating was measured using a FTÅ200.

The accelerated weathering testing was performed for 1000 h with a repeated cycle of 4 h of UV-A exposure at 60 °C followed by 4 h of water condensation at 50 °C.

Results and discussion

Hardness and flexibility of the polymer films. As shown in Figure 1 it can clearly be seen that the 2,2-dialkyl-1,3-propanediol based polycarbonate diols of 1000 g/mol provided very hard coatings with both exceeding the reference macrodiols in pendulum hardness. In addition to the high pendulum hardness Oxymer C112 displayed a very good flexibility as measured by the Erichsen flexibility, see Table 7. The macrodiol references also showed high flexibility but were a lot softer, with the polyether and polycaprolactone being the softest. The aluminium substrates break at approximately 6-7 mm. Therefore higher values could not be measured.

Very hard coatings are often associated with lower flexibility, as in the case of the BEPD polycarbonate, Oxymer M112. The lower flexibility of the BEPD polycarbonate could be explained by the shorter distance between the two hydroxyl groups of the macrodiol than the hexanediol based groups for example. Also the molecular weight of the macrodiols is approximately 1000 g/mol, and due to the higher molecular weight of BEPD, the number of the repeating units in the BEPD polycarbonate is lower.

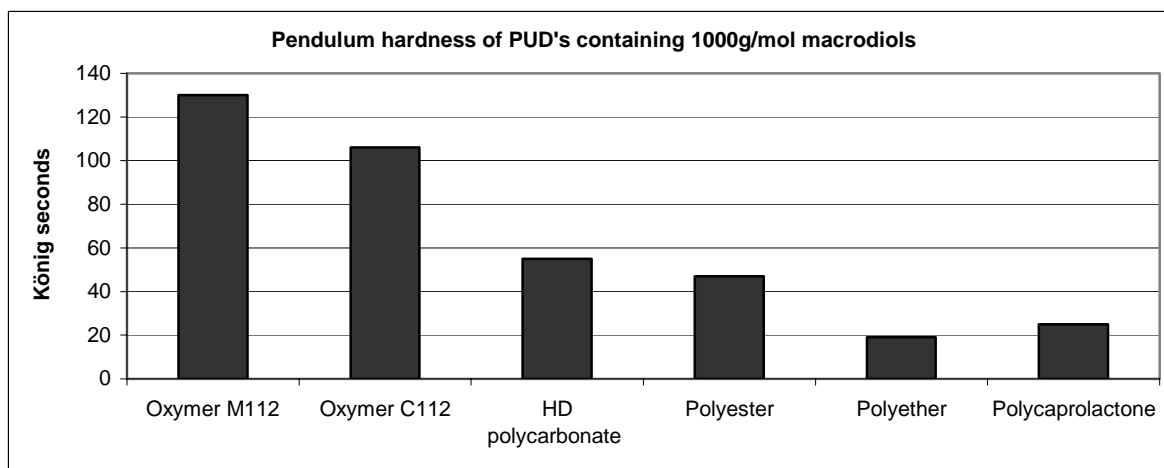


Figure 1. Pendulum hardness of force dried samples 24 h at 80 °C. Dry film thickness 25 $\mu\text{m} \pm 5 \mu\text{m}$.

Compared to the softer polyether, polyester and polycaprolactone references the PUD's containing the polycarbonate macrodiols all displayed significantly higher pencil hardness, see Table 7.

Table 7. Pencil hardness and Erichsen flexibility of the 1000 g/mol PUD's on clear coating after force drying 24 hours at 80 °C.

| Macrodiol 1000 g/mol | Pencil hardness | Flexibility (mm) |
|----------------------|-----------------|------------------|
| Oxymer M112 | 2H-3H | 1.0 |
| Oxymer C112 | F-H | 6.0 |
| HD polycarbonate | 2H-3H | 6.4 |
| Polyester | 2B-B | 6.2 |
| Polyether | 5B-4B | 6.2 |
| Polycaprolactone | 3B-2B | 6.5 |

The PUD's based on the higher molecular weight macrodiols displayed lower pendulum hardness values than their lower molecular weight counterparts. Despite the lower pendulum hardness, the Oxymer polycarbonate diols still gave higher hardness values compared to the PUD with hexanediol polycarbonate.

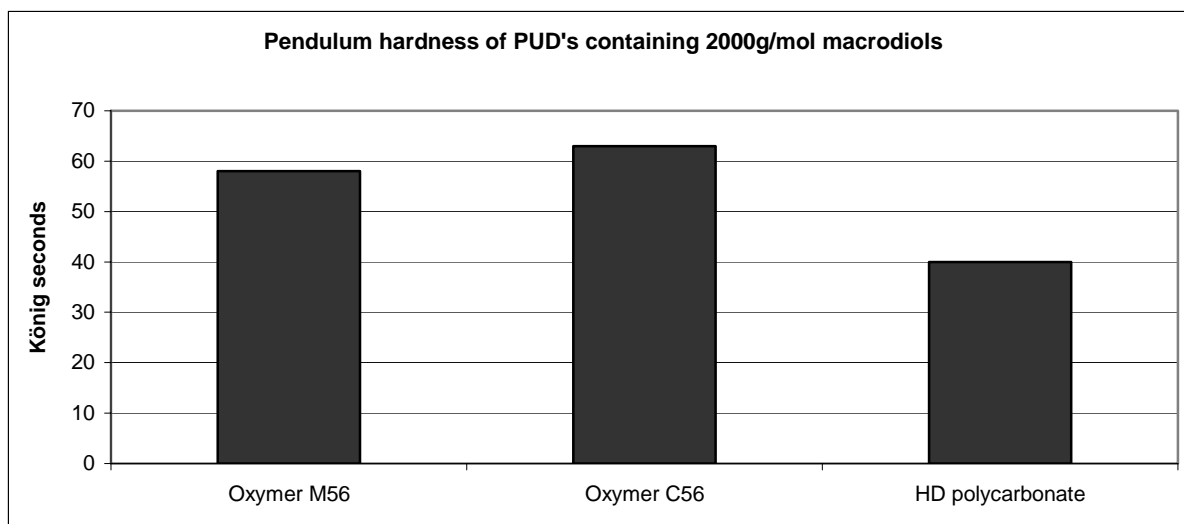


Figure 2. Pendulum hardness of force dried samples 24 h at 80 °C. Dry film thickness 25 $\mu\text{m} \pm 5 \mu\text{m}$.

The pencil hardness also decreased to some extent with an increased molecular weight of the macrodiol with the exception of the hexanediol polycarbonate which increased in value, see Table 8. With a molecular weight of 2000 g/mol the Oxymer M displays flexibility as good as the HD polycarbonate.

Table 8. Pencil hardness and Erichsen flexibility of the 2000 g/mol PUD's on clear coating after force drying 24 hours at 80 °C

| Macrodiol 2000 g/mol | Pencil hardness | Flexibility (mm) |
|----------------------|--------------------|------------------|
| Oxymer M56 | F-H | 6.3 |
| Oxymer C56 | F-H | 6.0 |
| HD polycarbonate | 4H-5H ¹ | 5.9 |

1. Difficult to evaluate due to rough surface

Adhesion. The adhesion on Aluminium was exceptional for all PUD's except the hexanediol polycarbonate based, where the adhesion was average, see Table 9. In general good adhesion was observed for steel polyamide and PVC. On ABS were all the references failed or had lesser good results, the Oxymer polycarbonates performed well. The PUD's with the overall best adhesion results were the two containing the Oxymer macrodiols followed by the polycaprolactone.

Table 9. Adhesion cross cut on various substrates (0-5, 0 = no loss of material) for 1000 g/mol PUD's

| Macrodiol 1000g/mol | Aluminum | Steel | ABS | Polyamide | PVC | Sum |
|---------------------|----------|-------|-----|-----------|-----|-----|
| Oxymer M112 | 0 | 1 | 2 | 1 | 1 | 5 |
| Oxymer C112 | 0 | 1 | 1 | 1 | 0 | 3 |
| HD polycarbonate | 2 | 1 | 5 | 2 | 1 | 11 |
| Polyester | 0 | 1 | 5 | 1 | 1 | 8 |
| Polyether | 0 | 3 | 5 | 2 | 1 | 11 |
| Polycaprolactone | 0 | 1 | 3 | 2 | 1 | 7 |

The same good results were also observed with an increased molecular weight of the macrodiols with the exception that the HD polycarbonate containing PUD performed much worse. It failed completely on all substrates except on PVC, see Table 10.

Table 10. Adhesion cross cut on various substrates (0-5, 0 = no loss of material) for 2000 g/mol PUD's

| Macrodiol 2000g/mol | Aluminum | Steel | ABS | Polyamide | PVC | Sum |
|---------------------|----------|-------|-----|-----------|-----|-----|
| Oxymer M56 | 0 | 0 | 1 | 0 | 0 | 1 |
| Oxymer C56 | 0 | 0 | 5 | 1 | 0 | 6 |
| HD polycarbonate | 5 | 5 | 5 | 5 | 1 | 21 |

Chemical resistance. As shown in Table 11 the polycarbonate diols performed much better overall than the polyester, polyether and polycaprolactone references in the chemical spot test evaluation. Very good resistance towards acidic and alkaline solutions was observed, except that the hexanediol based performed slightly poorer. The water resistance was excellent for the Oxymer macrodiols with the other macrodiols performing less well. Acetone is somewhat better for the all polycarbonate diols, although the resistance to ethanol is equally poor for all the coatings regardless of macrodiol used.

Table 11. Chemical resistance of the polymer films measured with spot test. Graded from 5-1 where 5 = no visible change and 1 = distinct mark and with an altered surface.

| Macrodiols 1000g/mol | Acetone 1 min | Water 16 h | Ethanol 2 min | HCl (aq, 5 %) 1 h | NaOH (aq, 5 %) 15 min | Sum |
|-------------------------|------------------|---------------|------------------|----------------------|--------------------------|-----|
| Oxymer M112 | 3 | 5 | 2 | 5 | 5 | 20 |
| Oxymer C112 | 3 | 5 | 2 | 5 | 5 | 20 |
| HD polycarbonate | 3 | 3 | 2 | 4 | 4 | 16 |
| Polyester | 2 | 2 | 2 | 4 | 3 | 13 |
| Polyether | 2 | 1 | 2 | 2 | 3 | 10 |
| Polycaprolactone | 2 | 1 | 2 | 2 | 3 | 10 |

The chemical resistance of the 2000 g/mol macrodiol based PUD's were lower compared to the 1000 g/mol macrodiol containing PUD's, especially towards water and sodium hydroxide, see Table 12. The Oxymer M56 polycarbonate due to its high hydrophobicity still showed excellent water resistance with the increased molecular weight.

Table 12. Chemical resistance of the polymer films measured with spot test. Graded from 5-1 where 5 = no visible change and 1 = distinct mark and with an altered surface.

| Macrodiols 2000g/mol | Acetone 1 min | Water 16 h | Ethanol 2 min | HCl (aq, 5 %) 1 h | NaOH (aq, 5 %) 15 min | Sum |
|-------------------------|------------------|---------------|------------------|----------------------|--------------------------|-----|
| Oxymer M56 | 2 | 5 | 2 | 5 | 4 | 18 |
| Oxymer C56 | 3 | 3 | 2 | 4 | 3 | 15 |
| HD polycarbonate | 2 | 2 | 2 | 4 | 2 | 12 |

Abrasion resistance. After 10 double rubs the Oxymer C112 PUD showed a similar reduction in gloss as the polycaprolactone whereas the hexanediol polycarbonate showed a much greater reduction, a decrease of almost 50 % in gloss was observed. After 50 double rubs the polycarbonate macrodiol with best gloss retention were found to be the coatings containing Oxymer C112, and the overall best performing macrodiol was the coating with the polycaprolactone, see Figure 3.

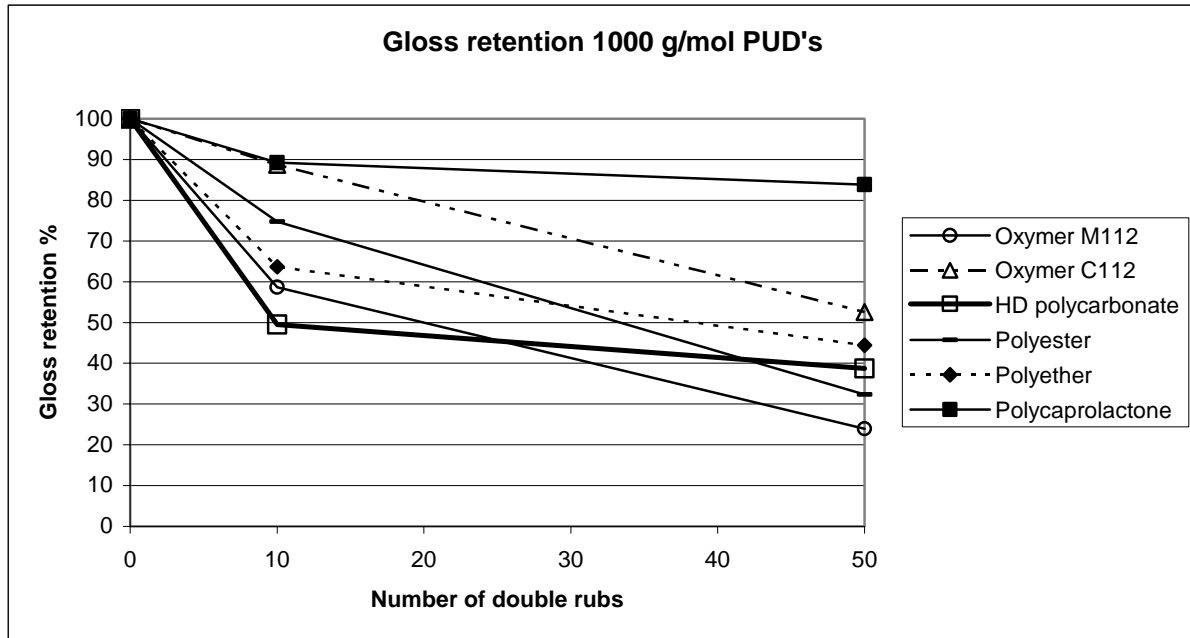


Figure 3. Scotch Brite™ abrasion resistance test; where the gloss retention is a measure of the abrasion resistance – the higher the gloss retention the better the abrasion resistance.

Surface tension. The contact angle of water drops on cured coatings is shown in Table 13 and Figure 4. From the contact angle images it can be clearly seen that Oxymer M112 exhibits a lower surface energy compared to the other coatings, i.e. it is the most hydrophobic. Oxymer C112 had a contact angle closer to the more conventional macrodiols. The low surface energy indicated by the high contact angle of the Oxymer M112 polycarbonate, could render this macrodiols ideal when applying coatings to e.g. plastic substrates.



Figure 4. Water drops on cured coatings of two of the PUDs.

Table 13. Contact angle of water drops on the surface of the coatings (1000 g/mol)

| Macrodiol | Contact angle ° |
|------------------|-----------------|
| Oxymer M112 | 74 |
| Oxymer C112 | 62 |
| HD polycarbonate | 54 |
| Polyester | 60 |
| Polyether | 62 |
| Polycaprolactone | 59 |

Weathering resistance. The weathering resistance of Oxymer M112 was compared to the hexanediol polycarbonate after an accelerated weathering test. The coatings were exposed for a total of 1000 hours to a varied climate of 4 hours of UV-A at 60 °C and 4 hours of condensation at 50 °C. In Figure 5 it can be seen that the hexanediol polycarbonate, after the full test cycle became white, whereas the BEPD polycarbonate was more or less unaffected. It could therefore be concluded that the BEPD based polycarbonate diol has better weather resistance than the hexanediol polycarbonate.

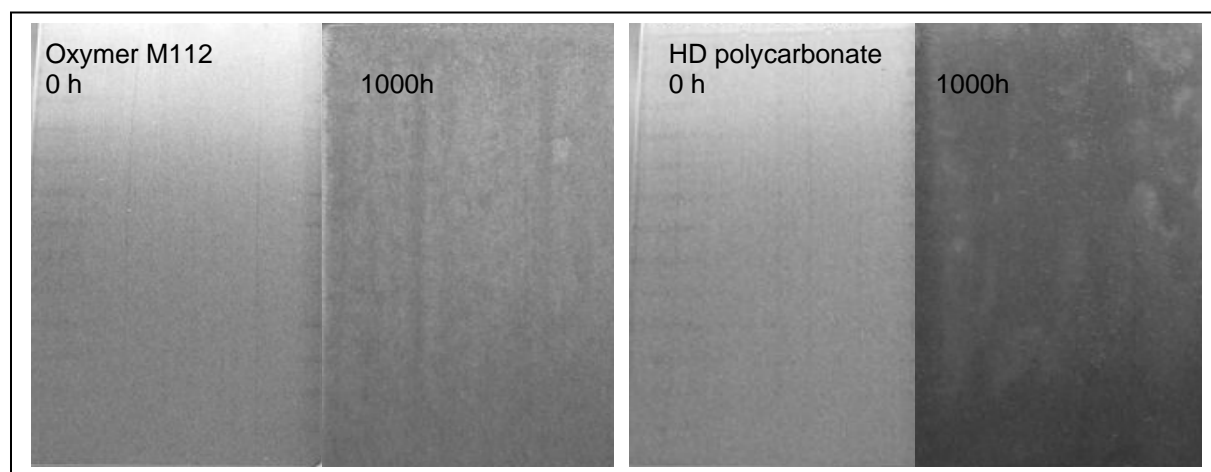


Figure 5. Accelerated weathering test. The two panels to the left are from Oxymer M112 before (left) and after 1000 hours of accelerated weathering (right). The two panels to the right are from the hexanediol polycarbonate before (left) and after 1000 hours of accelerated weathering (right)

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Conclusions

Oxymer® - a novel class of liquid aliphatic polycarbonates, developed by Perstorp AB was presented and evaluated in polyurethane dispersions. Coatings prepared from the PUD's were evaluated regarding hardness, flexibility, adhesion, chemical resistance and accelerated weathering and compared to a conventional hexanediol polycarbonate together with other macrodiols such as a polyester, polyether and polycaprolactone. These newly developed polycarbonates all show a high hardness, very good adhesion, excellent water, acid and base resistance and very good weathering resistance. In comparison to the traditional hexanediol polycarbonate the polycarbonate diols showed better hardness, adhesion, water, acid and base resistance and weathering resistance.