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HYDROPHOBIC POLYETHERAMINES FOR MOISTURE-RESISTANT POLYUREA COATINGS

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Polyurea systems have excellent performance and are therefore used in a broad variety of industrial applications. These include spray coatings that seal or cover roofs, pavement slabs for bridges, swimming pools, rail beds and tunnels.

Polyurea systems offer benefits in the segment of industrial flooring and sealants because, in contrast to other spray coatings, they may be applied in humid and low-temperature conditions and cure fast. As curing takes just seconds, waiting times are clearly reduced, for example in rehabilitation projects, which helps to cut the overall cost.

Chemically speaking, polyurea elastomers are polymers formed by an isocyanate prepolymer reacting with diamines that act as curing agents. The striking features of polyurea elastomers include their ability to readily bridge cracks with an elastic coating and their superb adhesion to a wide variety of surfaces.

They are also exceptionally resistant to chemicals, high temperatures and mechanical strain. Their adhesion to different types of material is illustrated by coating applications on concrete, steel, polyurethane foam and wood.

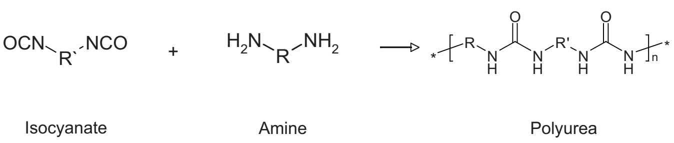
Polyureas consist of defined hard and soft segments as they are known in polyurethanes, a related material. By selectively adjusting these

segments, one can vary the properties of the polymer film over a broad range, from highly elastic and soft to hard and brittle.

To adjust the desired properties, formulators may choose from a selection of isocyanate prepolymers and, most importantly, from different types of polyetheramines that, when appropriately mixed with each other and combined with amine chain extenders, help the broad range of applications of these coatings.

With its polytetrahydrofuran amines (PolyTHF amine 1700, 350) (PTMG, C4 basis), BASF offers polyetheramines that are different from common amines based on polypropylene glycol (PPG, C3 basis) (Figure 2).

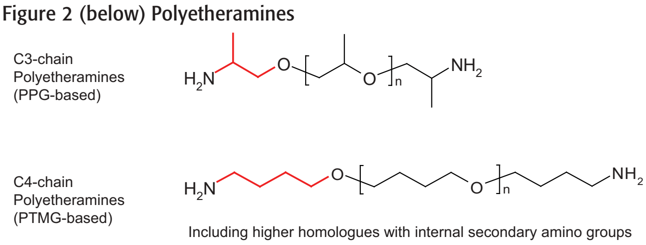
They aim to enhance properties like heat and humidity resistance. This approach is based on the success story of PolyTHF, or polytetramethylene glycol in chemical terms. PolyTHF is used as an amorphous soft segment in the manufacture of elastic textile fibers such as spandex or elastane fibres. The textiles made from these fibres remain highly elastic and are also resistant to high humidity over a broad range of temperatures.



- Very fast reaction for spray application
- No catalysts are needed

Figure 1 (above): The polyurea curing reaction. Component A: isocyanate oligomers and/or isocyanate prepolymers (aromatic & aliphatic systems used) Component B: Multifunctional amines or amine mixes, chain extenders, pigments, other additives.

Figure 2 (below) Polyetheramines



PolyTHF amines in polyurea coating

Although polyamines based on polytetramethylene glycol have been occasionally described in literature and although their use in polyurea systems has been recommended, hardly any experimental data can be found. Most importantly, a direct comparison of major elastomer properties between C3- and C4-based polyetheramines is missing.

Based on laboratory spray tests, this paper therefore studies whether and in what respects PolyTHF amines differ from PPG-based polyetheramines.

The tests were performed as follows: PSM 3000 type spraying machine by Isotherm; spray gun by Isotherm with a No 3 mixing chamber; 120 bar pressure; 70°C, 1:1 mixing ratio by volume; 1.05 index.

Because of its superior hydrophobic properties and linearity, the C4 polyetheramine was expected to contribute to enhancing the behaviour of the formulation in hot and humid conditions while improving or at least maintaining its mechanical properties.

Properties of PolyTHF amine 1700

C3 polyetheramine D2000, a di-functional primary amine with a molecular weight of about 2000, is proportionately the most important raw material in the curing agent component. Generally it is this polyetheramine, and mainly the longer-chain polyetheramines such as, in particular, the tri-functional polyetheramine T5000, that determine the elasticity of polyurea films.

PolyTHF amine 1700 has a molecular weight of about 1700 and, in addition to terminal primary amine functions, also contains a high percentage of internal secondary amine function, so it is also essentially tri-functional.

Table 1 shows the physical data of the individual polyetheramines. Table 2 gives the composition of the polyurea formulations tested. A standard formulation based on D2000, T5000 and DETDA (diethyltoluylenediamine) as a chain extender is compared to formulations in which T5000 was replaced with 10 percent and 20 percent PolyTHF amine 1700, respectively.

The same MDI prepolymer containing 15 percent NCO was used in all cases. To ensure comparability of the mechanical data, constant proportions of hard and soft segments were maintained (about 40 percent hard segment), and the amine component was adjusted according to the amine equivalent weight of

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its components.

Mechanical properties
The mechanical properties of the standard formulation and the formulations containing 10 percent and 20 percent PolyTHF amine 1700, respectively, were compared (Shore D hardness; tensile strength, elongation (DIN 53504 and DIN EN ISO 527); tear strength (DIN ISO 34-1); abrasion (DIN 53516), see Table 2. The comparison shows the latter to be significantly harder and less prone to abrasion. There is only a minor impact on elasticity. This is remarkable insofar as increased hardness is typically associated with a loss of elasticity.

Ageing tests in hot and humid conditions (90°C) – water absorption behaviour

The ageing behaviour of the formulations identified above was compared in a long-term experiment following DIN ISO 1817 by immersion in hot water at 90°C for various periods of time. As Figure 3 shows, the film obtained from the standard formulation takes up water continually during the test period of 35 days, up to a level of 5 percent by weight. In contrast to this, the formulations containing 10 percent and 20 percent of PolyTHF amine 1700, respectively, initially take up water but quickly reach a saturation limit at about 1.5 percent.

Reduced swelling can be assumed to mean a lesser risk of coating delamination in hot and humid climate conditions. This is due to the more hydrophobic character of the PolyTHF amine. No significant differences were observed between the PolyTHF amine levels of 10 percent and 20 percent.

Elongation behaviour after hot-water immersion

Along with water absorption, the elongation behaviour of the polyurea membranes treated as above was tested. Figure 4 shows that coating elasticity declines continually in all three formulations over the test period, but this process is clearly less pronounced in the PolyTHF amine formulations. Here again, the formulations with 10 percent and 20 percent of PolyTHF show only minor differences between them.

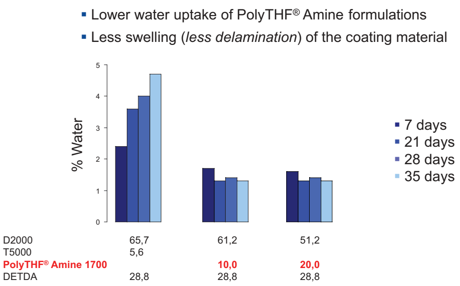
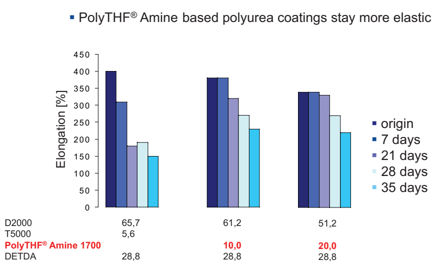


Figure 3: Ageing tests in hot/humid conditions (35 days, 90°C), water absorption behaviour

Figure 4 (below): Ageing tests in hot and humid conditions (35 days, 90°C), elongation behaviour



Elongation after immersion in different chemical media

In another experiment, the samples were exposed to chemical media of different polarity – ammonia (10 percent), diesel fuel and sulphuric acid (10 percent) – for seven days at 23°C. There were no significant differences in chemical resistance among all the

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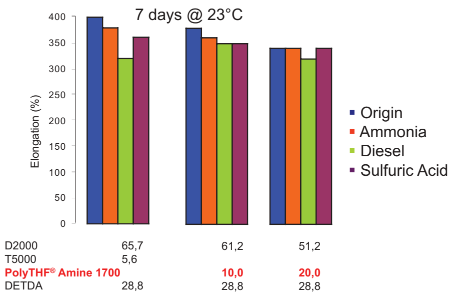

Figure 5: Elongation after immersion in various media (7 days, 23°C)

formulations. While obviously more hydrophobic, the PolyTHF amine formulations showed resistance results, even for diesel fuel, comparable to those of the standard formulations (Figure 5).

In conclusion, we found formulations containing PolyTHF amine 1700 (and adjusted for the same proportion of hard and soft segments) to produce harder, more abrasion-resistant films that those containing T5000, the increase in hardness being accompanied by hardly any loss of elasticity.

However, the major advantage of PolyTHF amine based formulations is the fact that they take up significantly less water and therefore show less swelling. This amine therefore helps to enhance the product properties mainly in humid environmental conditions. This is a major practical benefit, for example in rehabilitation of sewers and of sewage-treatment or water-treatment facilities, or in seawater-desalination plants.

Along with PolyTHF amine 1700, which is described here and was extensively tested, we also performed first tests on a shorter-chain variety, PolyTHF amine 350 (molecular weight about 350). Because this polyetheramine is clearly more reactive, any addition of more than 5 percent by weight results in processing problems. But up to this limit there appears to be a similar trend in results as for the longer-chain homologue.

Consequently, PolyTHF amine 350 can be recommended mainly for use in spray systems that are slower by nature, or that are applied manually.

Table 1 Comparison of major physical properties of PPG polyetheramines (C3) and PolyTHF amines with C4 backbone

	MW [g/mol]	(AHEW)[g/eq.]•	Viscosity [mPa.s]	Melting point [°C]
Polyetheramine D2000	2000	1000	273 @ 23°C	-29
Polyetheramine T5000	5000	1940	870 @ 23°C	-50
PolyTHF amine 1700	1700	approx. 670	500-650 @ 40°C	+25
PolyTHF amine 350	350	approx. 165	50 @ 20°C	-7

• Amine hydrogen equivalent weight

Table 2 Comparison of mechanical properties (at constant hard segment percentage)

		Standard	PolyTHF amine systems	
Component A				
D2000	**wt%**	65.7	61.2	51.2
T5000	**wt%**	5.6	-	-
DETDA	**wt%**	28.8	28.8	28.8
PolyTHF amine 1700	**wt%**	-	10.0	20.0
Component B				
MDI prepolymer (PPG 2000 based)	% NCO	15.0	17.0	17.0
(Hard segment content, %		40	42	42)
Shore D hardness		44	52	53
Tensile strength [MPa]		16	25	24
Elongation [%]		400	380	340
Tear strength [kN/m]		67	68	70
Abrasion [mm³]		187	145	150