Ultramid®, Ultradur® and Ultraform®

Resistance to Chemicals

Further information on individual products:

www.ultramid.de

www.ultradur.de

www.plasticsportal.eu/ultraform

We create chemistry

Basics

The following explanations should give an impression of the phenomena and influencing factors that can be met when thermoplastic components are exposed to chemicals. The statements made here are of a general nature and do not claim being complete or universally valid. Only in individual cases it is possible to adequately take into account all of the relevant factors and to assess the effects.

The consequences of exposing a polymeric material to various types of media can depend on many factors that sometimes interact in a complex way. Consequently, testing a component under realistic circumstances and under typical application conditions always gives the most meaningful results on whether a material is suited for a given application or not. In contrast, when it comes to laboratory tests, simple test specimens are often exposed to a medium under well-defined and constant conditions. Such experiments allow a relative comparison between different materials and thus lay the foundation for pre-selecting potential candidates as the right material for a given application. However, these experiments cannot substitute actual-practice testing.

Influence of processing on the resistance to media

Apart from the environmental conditions to which a component is exposed during its service life, all of the production and processing steps can also affect the quality of a component. Especially if environmental factors can be expected to cause damage to the material during later use, design as well as gentle and expert processing are particularly important aspects. After all, weak structural or qualitative spots usually mean that the material cannot withstand damaging environmental effects for longer, thus needlessly shortening the maximum service life.

Environmental effects

The environmental conditions for a component are essentially defined by the physical factors of temperature and pressure as well as by the chemical nature of the ambient medium. An ambient medium is fundamentally defined by its chemical composition. In fact, technical fluids often consist of one or two main components, together with several additives that are normally present in small concentrations. It can very well be that precisely these additives play a prominent role in the damage potential of a medium. It is not justified to transfer the test results of a medium 1 to a medium 2 that only matches the first one in terms of its main components. In the worst case, even impurities that are unintentionally present in the medium might be the decisive factor. This is especially the case when these compounds are catalytically active and thus could accelerate the damaging reactions.

It goes without saying that, in actual applications or in laboratory testing, not only the component undergoes aging but also the ambient medium. This aging process can be ascribed to chemical reactions in the medium and often goes hand in hand with the formation of chemical compounds that were not previously in the medium at all, or else only in small quantities. The statements made above also apply to the potential effects of these new compounds.

Media can act on a material or part in different ways. The boundary cases involving swelling, dissolution by solvents, reactions and stress crack formation will be briefly touched upon below.

Swelling

Swelling agents are media that a plastic can absorb in fairly large quantities and that then bring about changes in the properties of the part or material. For instance, the dimensions and weight of the component can change and, as a rule, so can the material properties such as stiffness, strength and toughness. The amount of swelling agent that can be absorbed is restricted by the saturation limit and so the plastic stays in solid form (these two factors distinguish swelling agents from solvents). Swelling is a physical process. The swelling agent and the plastic remain chemically unaltered in this process, they are simply present as a mixture. When it comes to partially crystalline polymers, swelling takes place practically only in the amorphous regions. If the ambient conditions change accordingly, then the swollen plastic can partially or completely release the swelling agent back to the surroundings. In this respect, swelling is a reversible process. However, once the swelling has occurred, the plastic will not be able to return completely to its original state. The reason for this is that swelling normally promotes relaxation or re-crystallization processes in the amorphous phase, so that the fine structure of the plastic changes slightly. Contact with swelling agents can be acceptable if the effect of the swelling agent does not jeopardize the functionality of the component.

The above-mentioned relaxation and re-crystallization processes can also be temperature-induced and can take place without the involvement of a medium. Temperatures above the glass-transition temperature promote this to a great extent. In many applications with partially crystalline polymers, the glass-transition temperature of the plastic is at least temporarily exceeded, sometimes even considerably. Here it should be noted that the glass transition temperature is reduced by swelling. Therefore, the tempering effects that occur in this process are fundamentally controllable.

Solvents

Solvents are media which, at a certain temperature, are capable of forming a liquid solution with a plastic. Whether a given medium is a solvent or not is highly dependent on the temperature. In the case of partially crystalline materials, a solvent has to be able to break up the crystalline structures of the polymer. As a rule, the closer this is to the melting temperature of the polymer, the easier this becomes.

In order to dissolve a polymer, especially with weak solvents, there is a need for larger quantities of solvent and a certain amount of time. In other words, brief contact of a component with small amounts of a potential solvent can be acceptable. The consequences are then similar to those described in the section on swelling. In this context, it is advantageous if the solvent is volatile and if the wetted site can easily dry again. Prolonged contact with larger quantities of solvents should be avoided under all circumstances.

Reaction between the ambient medium and the plastic
Whenever reactions occur between the ambient medium and the plastic, the extent of the resultant material changes must not exceed the acceptable limit. This is the case whenever the chemical reactions take place at such a low conversion rate that the part still works, even at the projected end of its service life.

Either directly or indirectly, chemical reactions normally cause splitting of the polymer backbone, that is to say, the polymer chains are shortened. Depending on the duration of these reactions, this can also lead to complete degradation of the polymer. The degradation products range from shorter-chain polymers to low-molecular-weight compounds which no longer have any of the properties of the original polymer.

Many material properties depend on the length of the polymer chains, but the individual properties by no means respond identically or simultaneously to changes in the chain length. Consequently, a universal definition of a limit for the end of the service life of components cannot be given.

Whether chemical reactions with a medium are more likely to occur in a boundary layer near the surface or throughout the entire volume of the part depends largely on how quickly the reactions take place (the reacting medium is consumed in this process) and how quickly fresh medium comes in again through diffusion from the outside. A reaction that is fast in comparison to the rate at which the medium is re-supplied promotes local damage that starts on the surface and can penetrate from there into the material. The damage is then diffusion-controlled. In contrast, a reaction that proceeds slowly in comparison to the rate at which the medium is re-supplied can cause damage that occurs uniformly throughout the entire volume of the part.

The higher the temperature and the higher the concentration of reactants (in other words, the plastic and the medium), the faster simple chemical reactions take place. For this reason, plastics that absorb a given medium in trace quantities or practically not at all can show a relatively high resistance to that medium. This, however, does not prevent possible damaging reactions on the surface.

Stress crack formation
Media that trigger stress crack formation are media that cause cracks to form within a relatively short period of time in a component that is under mechanical stress. As a rule, the media that trigger stress crack formation differ from one class of polymers to another. Partially crystalline polymers are less susceptible to stress crack formation than amorphous polymers are. The resultant cracks can have macroscopic dimensions and can cause the part to break.

Mechanical stresses can be caused by external forces or they can be due to internal stresses. These internal stresses are caused mainly by the local cooling processes, which always vary widely during injection molding since the layers close to the edges cool faster than those far from the edges. Since faster cooling often goes hand in hand with less shrinkage, layers that shrink differently can be formed. They are then under stress with respect to each other (compressive stress in the edge area and tensile stress in the core area).

Crack formation can take place with or without the occurrence of chemical reactions. Stress crack formation can be local and can even occur after exposure to very small quantities of the media in question. Therefore, contact with media that trigger stress crack formation is particularly critical and should be avoided. If such contact with a medium that triggers stress crack formation cannot be completely avoided for specific reasons, then care should already be taken during the design phase to ensure that the components are stress-free. Besides, it is advisable to use specially modified materials that, within their polymer class, are as impervious to stress crack formation as possible.

The viscoelasticity of plastics

As a rule, plastics, especially thermoplastics, show viscoelastic behavior that should not be neglected for the application in question. In other words, components that are under an external load (stress) show irreversible time-dependent and temperature-dependent plastic deformation (creep). The example in Figure 1 shows two creep curves for Ultraform® S2320 003. In air at a temperature of 80°C [176°F] and at an external tensile stress of 9 MPa, this material has total elongations (sum of elastic and plastic elongation components) of less than 2%. When in contact with FAM-B fuel (DIN 51604), which is a highly swelling medium for Ultraform®, the plastic is extensively deformed in spite of the low temperature (60°C [140°F]). This usually means that the part will fail prematurely.

Thermoplastic materials with reinforcing fillers (e.g. glass fibers, Figure 2), a high crystalline fraction, a high molecular weight and a glass-transition temperature above the application temperature are less susceptible to creep.

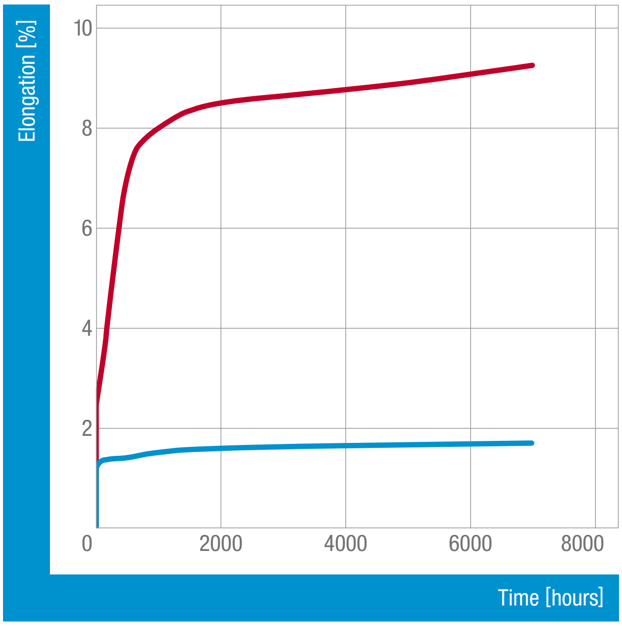


Figure 1: Tensile creep test for Ultraform® S2320 003 at 80°C [176°F] in air (blue curve), and at 60°C [140°F] in FAM-B fuel (red curve) at a tensile stress of 9 MPa

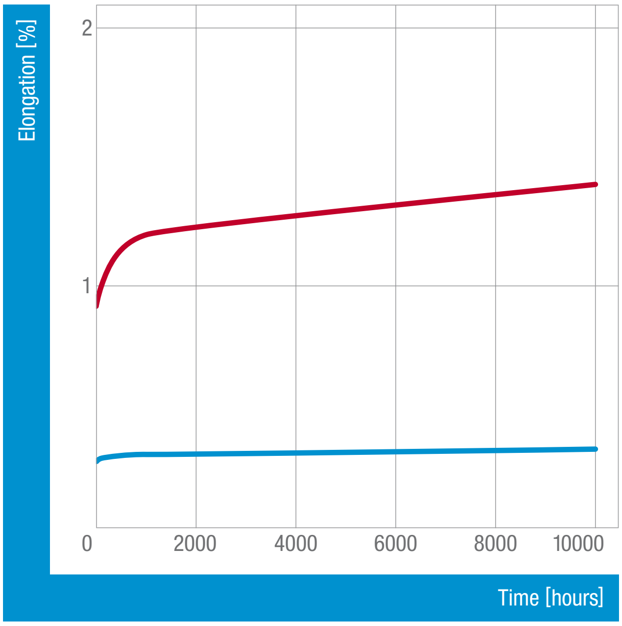


Figure 2: Tensile creep test for Ultradur® B4300 G6 bk Q16 15007 at 60°C [140°F] in air (blue curve), and in FAM-B fuel (red curve) at a tensile stress of 15 MPa

Short-term media resistance of Ul

The term short-term media resistance generally means that the surface and the properties of a plastic component should not change considerably in response to one-time contact with a chemical for one hour to a few hours at moderate temperatures. For instance, this is simulating the spilling of small amounts of operating fluids such as motor oil or battery acid in the engine compartment of a vehicle during the filling procedure. After a certain exposure time, the part in question is inspected for changes to its surface such as discoloration or cracks. If such changes are not visible, the material is classified as being resistant. The selection of the chemicals and the boundary conditions differ depending on the locationof the plastic part and on the OEM. The following example is typical for these requirements.

- Part: cylinder head cover made of Ultramid® A3WG6 bk 564
- Short-term contact: the surface is wetted with a drop of fluid; after a waiting time of 6 hours in a standard laboratory atmosphere, it is wiped off and inspected
- Typical contact points (Figure 3): area of ribs, radii and inserts

The test results are compiled in Table 1. This example shows that many operating fluids for automobiles (except for acids) are not critical for Ultramid® (Figure 4) during short-term contact.

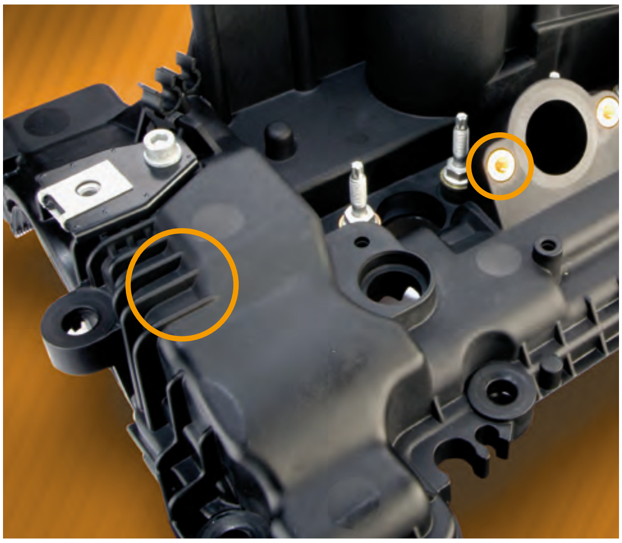


Figure 3: Typical contact points for testing short-term media resistance.

Figure 4: Visible surface damage after short-term contact with sulfuric acid (2 %).

Table 1: Test results for a component made of Ultramid® after short-term contact with various chemicals.

Test fluid	Test result
Coolant Glysantin® Protect Plus	No visible surface damage
Brake fluid DOT 4	No visible surface damage
Windshield cleaning fluid Sonax® AntiFrost & KlarSicht	No visible surface damage
Sulfuric acid (2 %)	Visible surface damage (Figure 4)
Diesel fuel	No visible surface damage

Additionally, for purposes of testing the short-term chemical resistance, stress cracking resistance tests are made with the bent strip method, for instance, analogously to DIN EN ISO 22088-3. In this test, tensile bars are clamped onto radius gauges that cause a defined strain of the outer fiber of, for example, 1% or 2%. Afterwards the test set-up is wetted with a chemical for several hours and subsequently visually inspected for cracks in case failure due to fracturing has not occurred.

The following example shows a typical result of the stress crack resistance test by means of the bent strip method (Figure 5).

Comparison of the materials: Ultradur® B4300 G6 and Ultradur® B4330 G6 HR. Grade B4330 G6 HR is optimized with special additives for particularly demanding environmental conditions while grade B4300 G6 does not have such additives.

Test procedure: injection-molded test specimens are clamped onto the bending gauge and brushed every 10 minutes with a 10% sodium hydroxide solution for a period of one hour and, at the same time, they are inspected for cracks. At the end of the hour, test specimens that have not fractured remain clamped without additional wetting with the solution for 24 hours, after which they are once again assessed. The test results are compiled in Table 2.

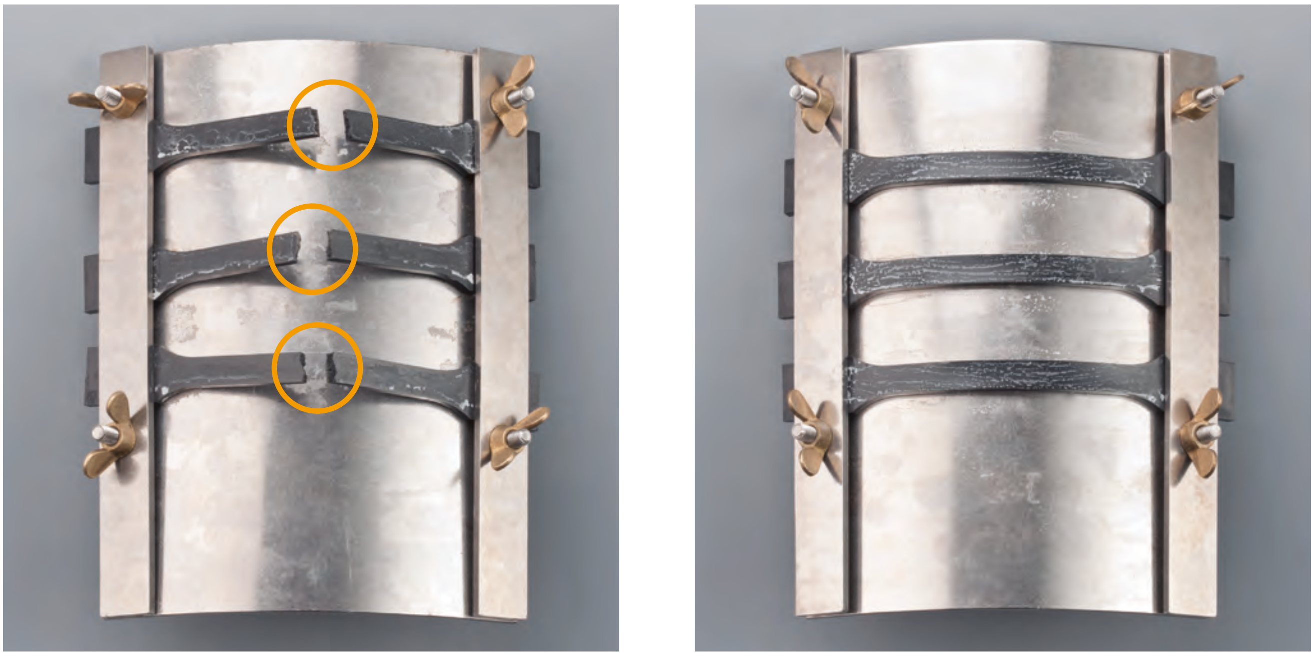


Figure 5: Stress crack resistance test by means of the bent strip method, conducted analogously to DIN EN ISO 22088-3; Ultradur® B4300 G6 bk 5110 on the left and Ultradur® B4330 G6 HR bk 15045 on the right.

Table 2: In the bent strip test, Ultradur® B4330 G6 HR shows improved stress crack resistance in contact with sodium hydroxide solution.

Product	Time [minutes]						Time [hours]
	10	20	30	40	50	60	24
Ultradur® B4330 G6 HR bk 15045	✓	✓	✓	✓	✓	✓	✓
Ultradur® B4300 G6 bk 5110	✓	✓	✓	x	x	x	x*

✓ no stress cracking
x visible stress cracking
x* all specimens fractured before 24 hours had passed

Long-term media resistance of Ul

In an evaluation of the long-term media resistance, products made of Ultramid®, Ultradur® and Ultraform® were exposed to the medium in question for at least a few weeks. After the period of exposure, the material was examined for changes. As a rule, exposure to the media was performed as follows:

- Use of standard test specimens: tensile bars of type 1A according to ISO 527-2 and/or flexural impact bars of type 1 according to ISO 179-1/-2.
- The standard test specimens were put in place immediately after having been injection-molded, that is to say, dry, and were then completely surrounded by the liquid medium; the test specimens should be positioned in such a way that they do not touch the vessel walls or each other and are not subjected to any external stress; only test specimens made of the same material must be kept in a given test vessel.
- The test vessel, preferably made of glass, is inert with respect to the medium. It is configured with a reflux condenser with which the atmospheric pressure is equalized; transparent test vessels are covered with aluminum foil to protect them against intense incident light.
- Autoclaves are used if the media temperatures are above the boiling point.
- The test vessels are heated by an adjustable heat source and the temperature of the medium is preferably measured with an internal thermometer.
- The test specimens are removed at room temperature, any media that might still be adhering to them are wiped off with a cloth; the properties are determined immediately after the test specimens have been removed.
- The tensile properties are determined in accordance with ISO 527-1/-2 and the Charpy impact properties according to ISO 170-1/-2 at +23 °C [+73.4 °F] on at least three, preferably five, test specimens per instance of removal.

The figures in chapter 3 show the course over time of the material properties for **long-term media contact**. Accordingly, the time intervals between two measuring points (= instances of removal) were considerably longer in comparison to those of chapter 2 (evaluation of the short-term media resistance). Whenever a material changes considerably in its properties over a **short time span**, certain deviations can occur between the actual and the shown course of the properties. This is particularly true of the swelling at the beginning of the exposure period. However, this does not have a negative impact on the quality of the measured curves for the evaluation of the long-term media resistance of the materials.

Aliphatic and aromatic hydrocarbons

Aliphatic hydrocarbons are organic compounds that consist of carbon and hydrogen and that are non-aromatic. The simplest representatives include the alkanes (e.g. methane, ethane, propane), cycloalkanes (e.g. cyclopentane, cyclohexane), alkenes (e.g. ethylene, propylene) and alkines (e.g. acetylene).

The parent and one of the most important representatives of aromatic hydrocarbons is benzene. Other compounds that are derived from this substance and that have the benzene skeletal structure as a structural feature also belong to the aromatic hydrocarbons. Important members of this class are the alkyl-substituted benzenes, for instance, toluene, the various isomeric forms of xylene and the so-called polycyclic aromatic hydrocarbons, for instance, naphthalene.

In technical applications, Ultramid®, Ultradur® and Ultraform® often come into contact with mixtures of aliphatic and aromatic hydrocarbons:

- fuels (Otto fuel, diesel), greases, lubricants, motor oils, non-water based coatings and paints
- natural gas (the main component being methane, along with ethane and higher alkanes)

Ultramid®, Ultradur® and Ultraform® show good resistance to the most common aliphatic and aromatic hydrocarbons and their mixtures, which are often met in technical applications.

Otto fuel

Ultramid® offers good resistance to Otto fuel, which is illustrated in Figure 6 for the example of glass-fiber reinforced Ultramid® A and B. However, it should be noted that ethanol and methanol fractions in gasoline (fluid N) cause severe swelling of polyamide; this is not the case for pure Otto fuel (fluid C), which is extracted from petroleum. Consequently, the aspect of dimensional stability is often more critical than that of chemical resistance. This example uses reference fuels according to DIN ISO 1817, Appendix A.

- Fluid C
  (mixture of 50 % 2,2,4-trimethyl pentane and 50 % toluene)
- Fluid N
  (mixture of 90 % Fluid C, 7 % ethanol, 3 % methanol)

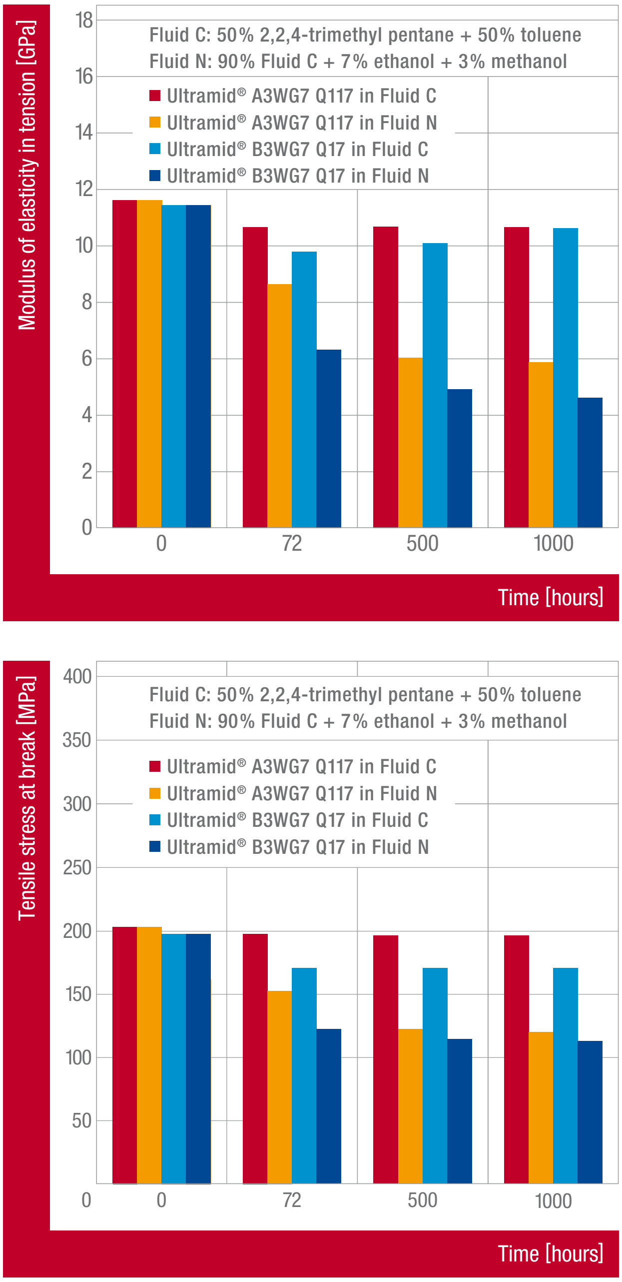


Figure 6: Resistance of Ultramid® A and B to Otto fuel at 70 °C [158 °F]; the alcohol fractions in the gasoline cause swelling.

Long-term media resistance of Ul

Ultraform® S1320 003 and Ultraform® S2320 003 show high resistance at 70 °C [158 °F] in Shell V-Power, a high-octane Otto fuel. The modulus of elasticity and the tensile strength of both materials stay at a constant high level after swelling at the beginning of the exposure time, which is associated with a 2 % fuel absorption (Figure 7).

Ultraform® S1320 003 has a lower co-monomer content than Ultraform® S2320 003. This results in increased crystallinity and thus greater stiffness and strength.

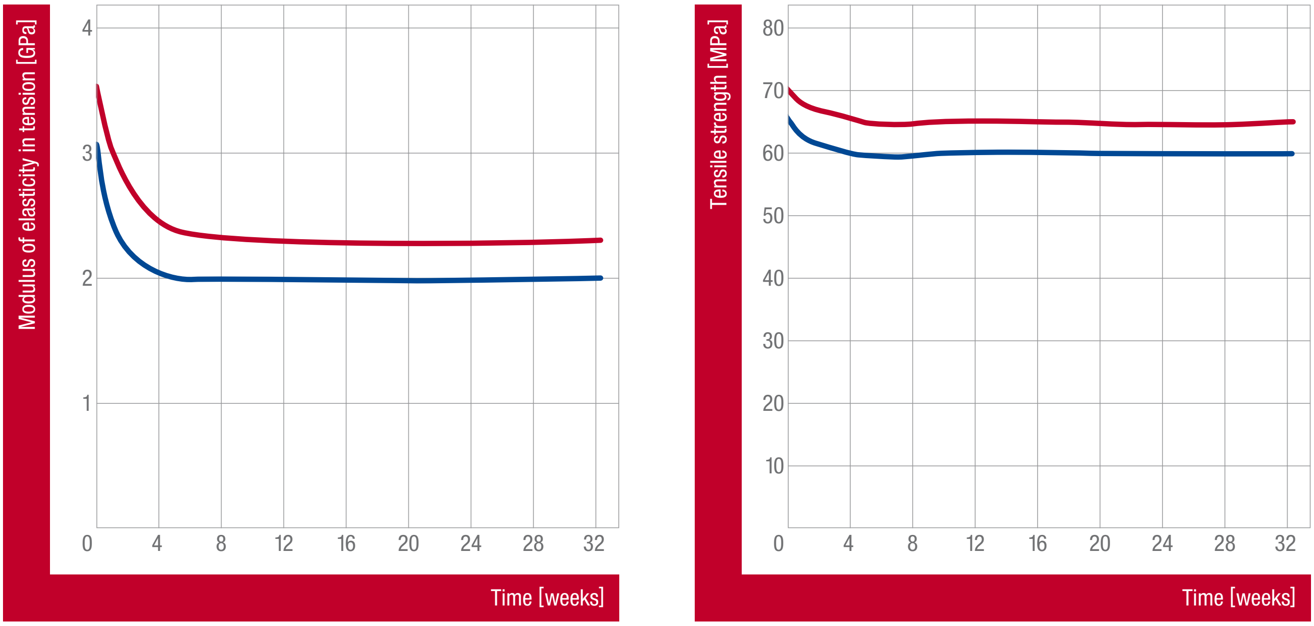
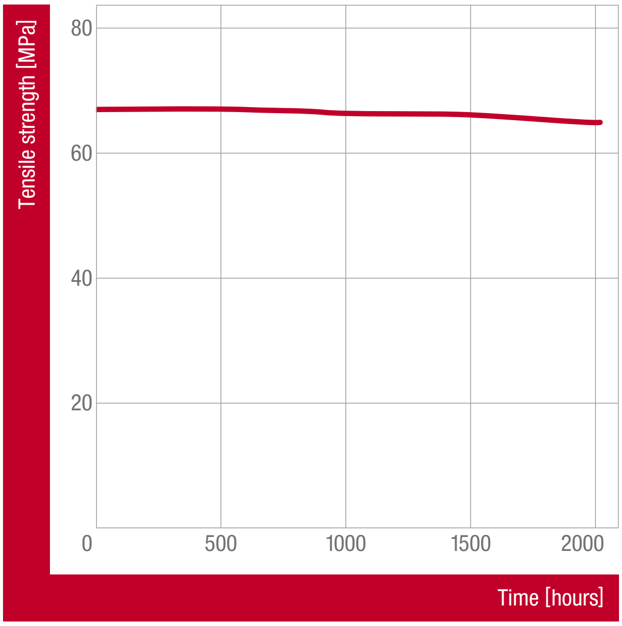


Figure 7: Exposure of Ultraform® S1320 003 (red curve) and Ultraform® S2320 003 (blue curve) to Shell V-Power at 70 °C [158 °F].

Diesel fuel

The example in Figure 8 shows the exposure of Ultraform® S1320 0021 to a diesel fuel at 100 °C [212 °F]. Ultraform® S1320 0021 is a grade that has been specially stabilized against hot diesel and aggressive fuels. The swelling in the used diesel test fuel made by Haltermann is a mere 0.8 %. Consequently, the modulus of elasticity of the fuel-saturated material only drops slightly. In contrast, there is virtually no loss in strength over the entire test period of 2,000 hours.

The excellent fuel resistance of Ultraform® has led to its long-standing success in the automotive industry, for example, for fuel tank covers, for components of fuel-carrying modules (Figure 9) as well as for tank vents (roll-over valves).



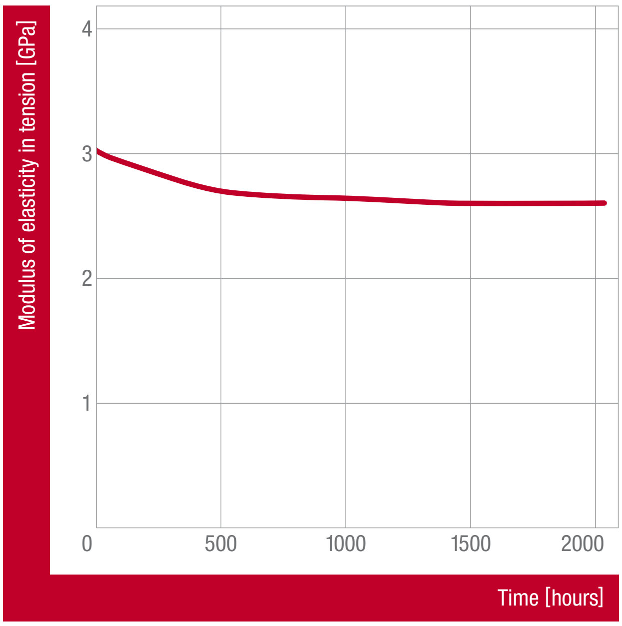


Figure 8: Exposure of Ultraform® S1320 0021 to Haltermann Diesel CEC RF 90-A-92 at 100 °C [212 °F].

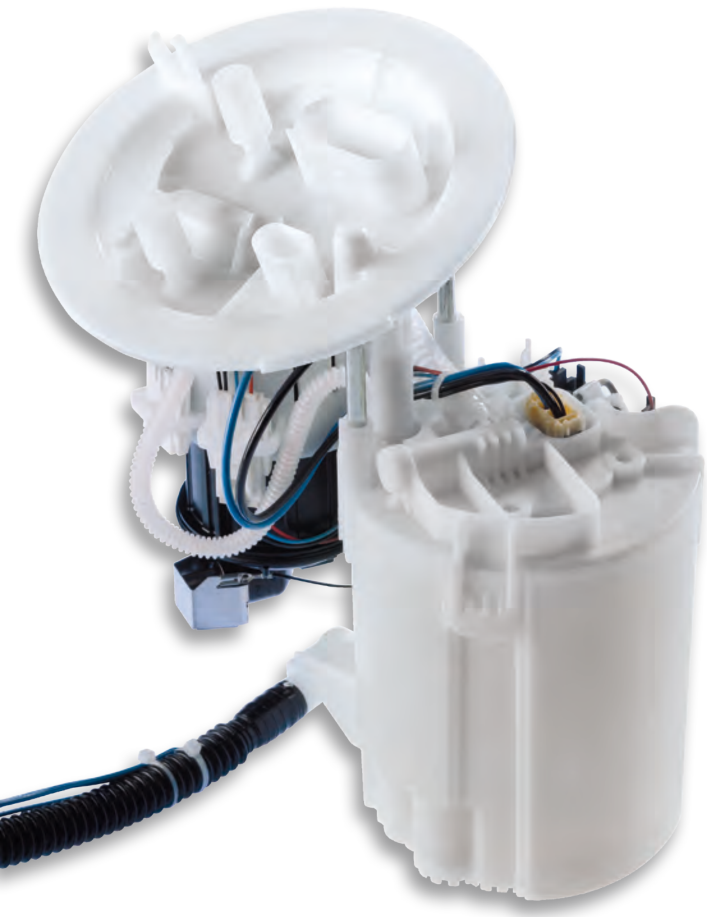
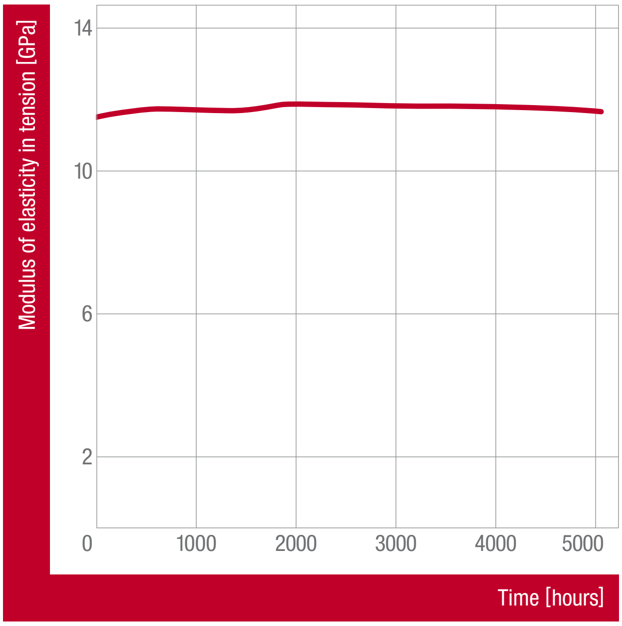


Figure 9: Fuel tank module made of Ultraform® S2320 003

Long-term media resistance of Ul



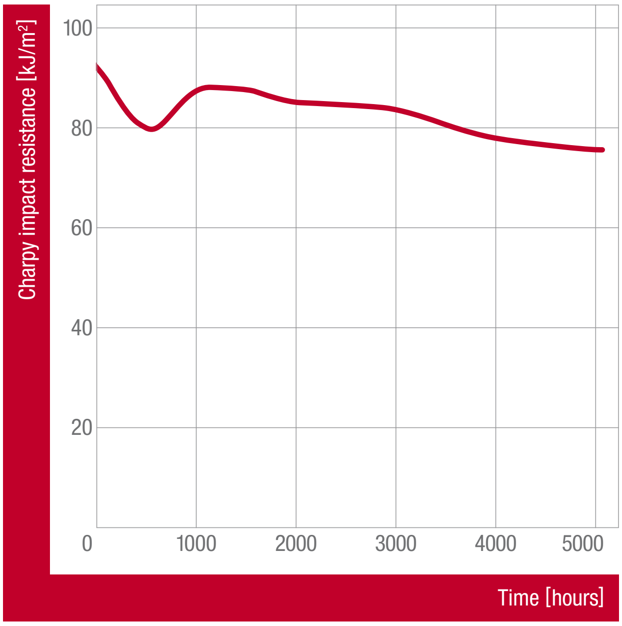
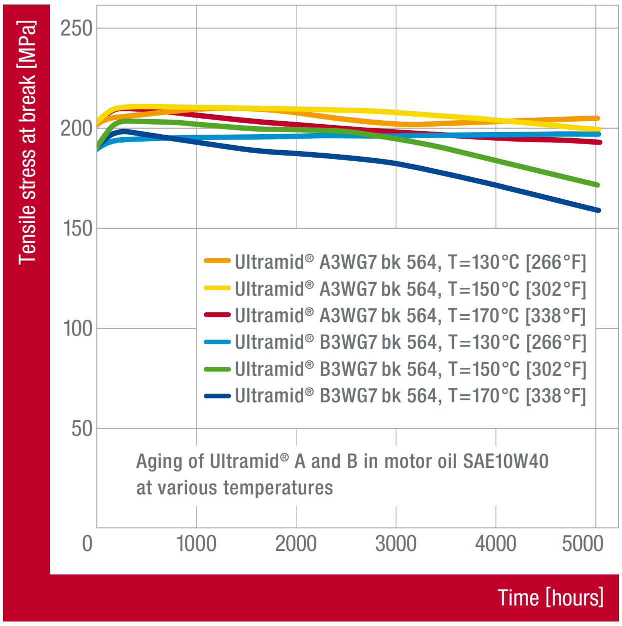


Figure 10: Exposure of Ultramid® TKR 4355G7 bk 564 to diesel fuel ASTDM D975 2-DS 15 at 100 °C [212 °F].

Thanks to its more polar molecular structure, Ultramid® is generally more resistant to non-polar diesel fuels (without the admixture of biodiesel) than Ultraform® is. The partially aromatic Ultramid® TKR 4355G7 bk 564 in its saturated state absorbs less than 0.1% of the diesel fuel. The modulus of elasticity, the tensile strength and the tensile strain at break remain practically unchanged over the course of 5,000 hours (Figure 10). Only the Charpy impact strength in the unnotched test bar drops slightly. Ultramid® TKR 4355G7 bk 564 is used, for example, in fuel pressure sensors (Figure 11).

Ultramid® A and B also show similarly good resistance to diesel fuel. This, however, only applies to a limited extent to biodiesel; see the section on esters.

Figure 11: Fuel pressure sensor made of Ultramid® TKR 4355 G7 bk 564.



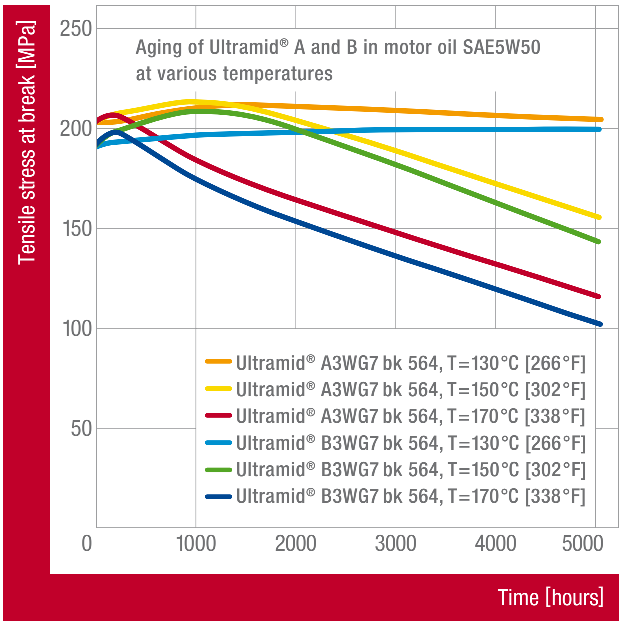


Figure 12: Resistance of Ultramid® A and B to various types of motor oil at high temperatures; the typical limit of the application range of motor oil is about 150 °C [302 °F].

Motor oil

Generally speaking, Ultramid® has an outstanding resistance to hot motor oil, as can be seen in Figure 12 for Ultramid® A3WG7 and Ultramid® B3WG7 bk 564 for the example of exposure to two different types of oil at high temperatures. The usual exposure temperature is 150 °C [302 °F] at the maximum. Data at higher temperatures is used in order to predict the behavior over prolonged operating times. At the typical exposure temperature of 150 °C [302 °F], the material still keeps more than 75 % of its initial strength, even after 5,000 hours. The influence exerted by the two types of oil on the behavior of the material differs markedly, which also confirms the need to carry out testing individually. The slight rise in the tensile strength at the beginning of the exposure period is due to post-crystallization of the product. It should be pointed out that the envisaged resistance at such high temperatures can only be achieved by materials that have been sufficiently heat-stabilized (for instance, as given in Figure 12 and 13).

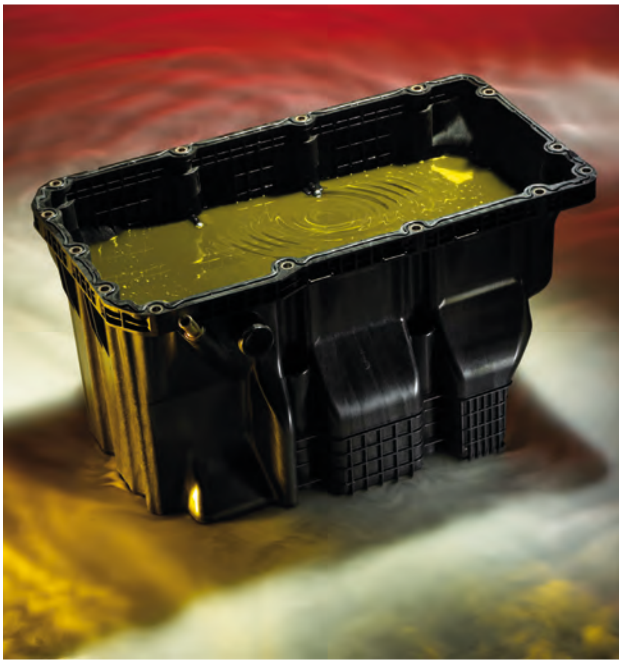


Figure 13: Motor oil pan made of Ultramid® A3HG7 Q17.

Long-term media resistance of Ul

Greases and lubricants

Many technical greases and lubricants are based on mineral oil or synthetically manufactured hydrocarbon oils that have been thickened with metal soaps (e.g. calcium stearate, lithium stearate). The Ultradur®, Ultraform® and Ultramid® grades often show good resistance to such greases, even at elevated temperatures. As a rule, the user is not aware of the precise compositions of such lubricants. For this reason, it is recommended that a test be carried out in any case with the greases that are actually going to be used.

The unreinforced Ultramid® A4H has been successfully used in contact with lubricating grease for many years.

The behavior of Ultradur® B4300 G6 bk 5110 at 100 °C [212 °F] with respect to hydrocarbon-based greases is shown in Figure 15.

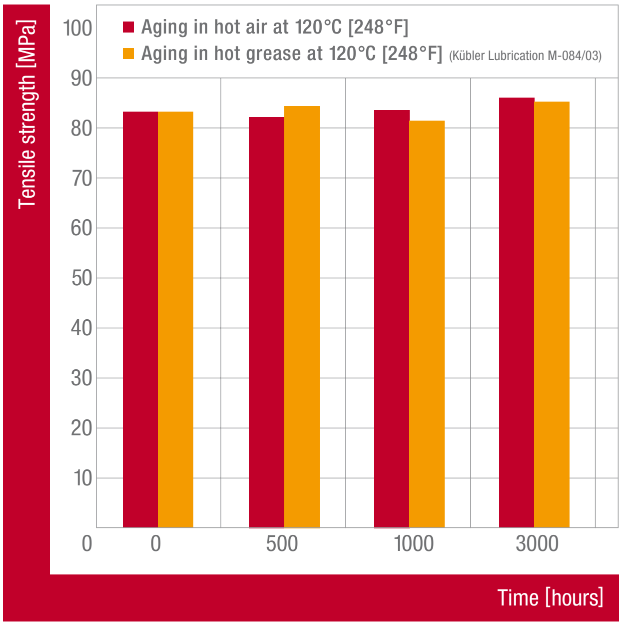


Figure 14: Resistance of Ultramid® A4H to grease at 120 °C [248 °F].

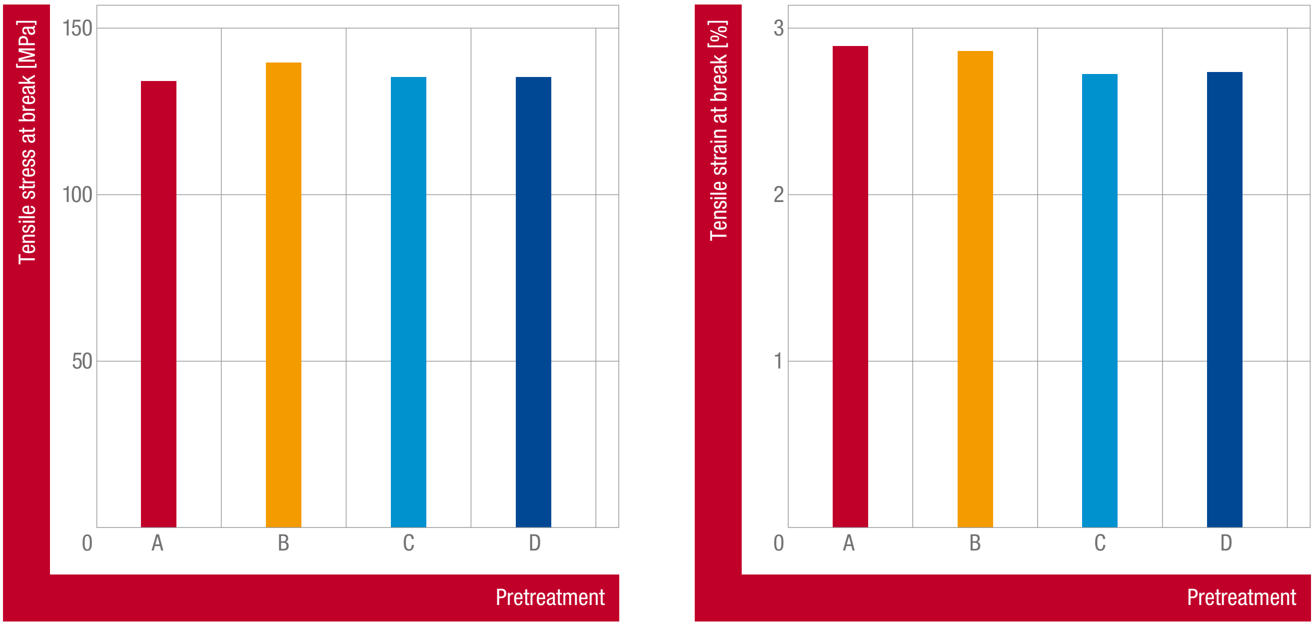


Figure 15: Mechanical characteristic values of Ultradur® B4300 G6 bk 5110 as a function of the pretreatment.
A: initial condition, freshly injection-molded
B: aged for 1,000 hours in hot air at 100 °C [212 °F]
C: aged for 1,000 hours in hot lubricating grease at 100 °C [212 °F] (synthetic oil, thickened with barium soap)
D: aged for 1,000 hours in hot lubricating grease at 100 °C [212 °F] (synthetic oil, thickened with lithium soap)

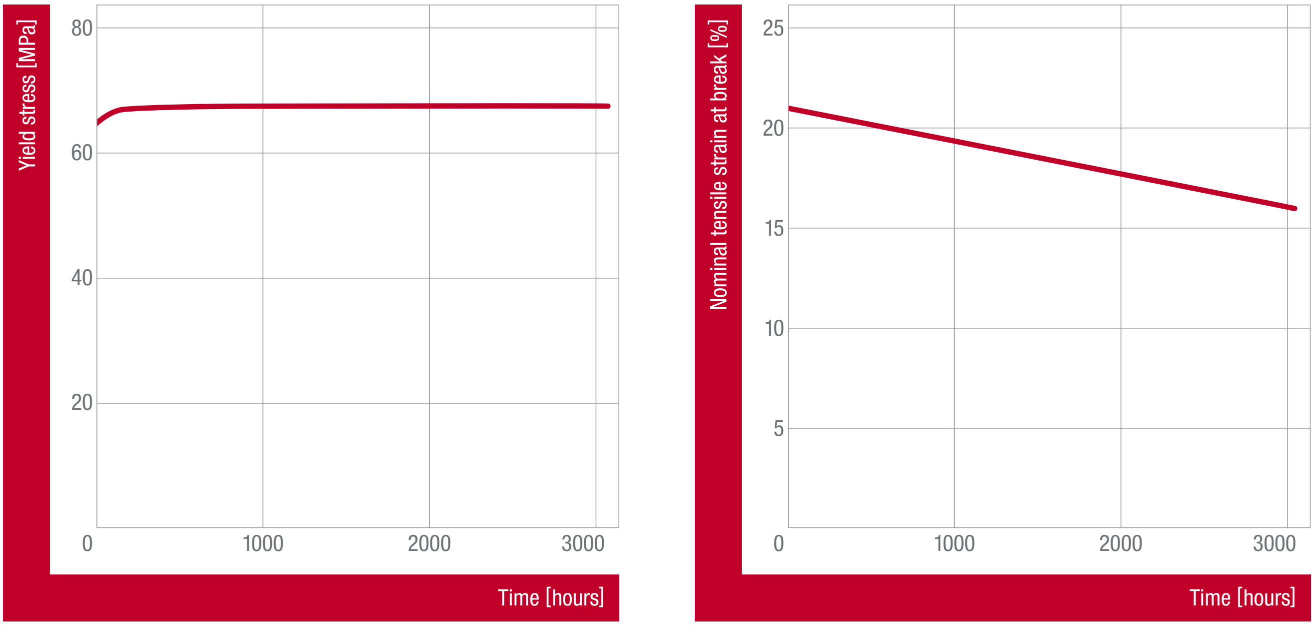


Figure 16: Resistance of Ultraform® N2320 003 bk 120 to a hydrocarbon-based lubricant[1], at 80 °C [176 °F].

The example in Figure 16 shows the resistance of Ultraform® N2320 003 bk 120 to a hydrocarbon-based lubricant, at 80 °C [176 °F].

Alkalis

Alkalis are substances that form alkaline solutions with a correspondingly high pH value when they come into contact with water.

Ultramid® offers good resistance to alkalis and alkaline solutions, although hydrolytic splitting of the amide groups can occur upon contact. The reaction rate at room temperature, however, is so low that no noteworthy damage occurs to the polymer.

For instance, after the swelling process has ended, Ultramid® A3EG7 in a 10 %-aqueous solution of ammonia shows only a moderate drop in strength within one year at 60 °C [140 °F] (Figure 17).

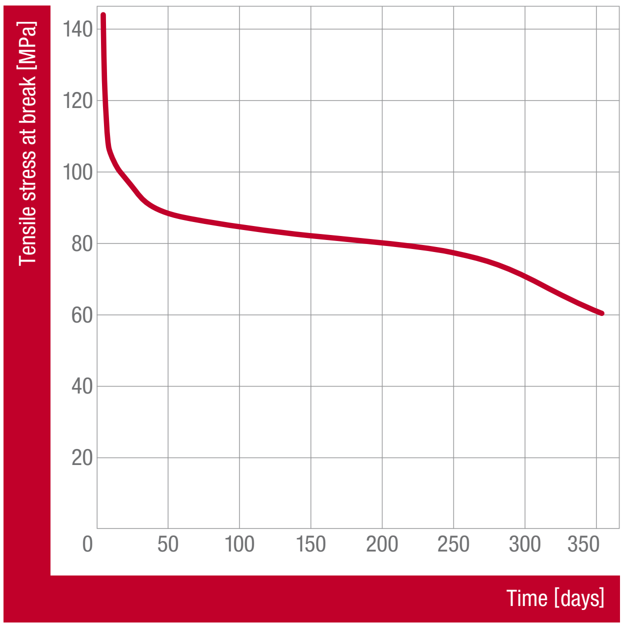


Figure 17: Exposure of Ultramid® A3EG7 to a 10 %-aqueous solution of ammonia (pH 13) at 60 °C [140 °F].

[1] type 571 made by Innotec Vertriebs GmbH

Long-term media resistance of Ul

Examples of applications in which Ultramid® has proven its worth for years include the following:

- plastic wall plugs in contact with concrete
- housings[2] for batteries that are operated with potassium hydroxide solution (Ultramid® B)
- SCR modules[3] in which the materials come into contact with an aqueous urea solution (Ultramid® A)

When glass-fiber reinforced polyamides are used, it should be kept in mind that contact with alkaline media damages the glass fibers and causes a deterioration of the mechanical properties.

Ultraform® offers good resistance to alkaline media. In the case of glass-fiber reinforced Ultraform® grades such as Ultraform® N2200 G53, the same is true as for glass-fiber reinforced Ultramid®.

Figures 18 and 19 show examples of the exposure of Ultraform® N2320 003 and Ultraform® N2200 G53 to the alkaline medium AdBlue®, an approximately 33%-aqueous solution of urea, at 60°C [140°F].

Figure 20 shows the tensile strength of Ultradur® B4300 G6 when exposed to aqueous sodium hydroxide solutions (caustic soda solution) at room temperature. The change in the tensile strength or the damage to the material depends to a great extent on the pH value. Whereas the material undergoes practically no drop in strength for up to 500 hours at a pH value of 10, the strength already drops after a very short time at a pH value of 14; after 200 hours, the material only exhibits one-fifth of its initial strength.

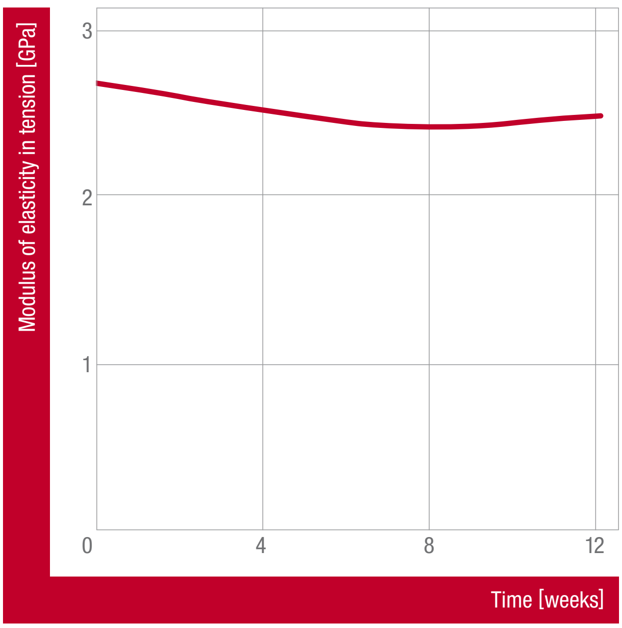
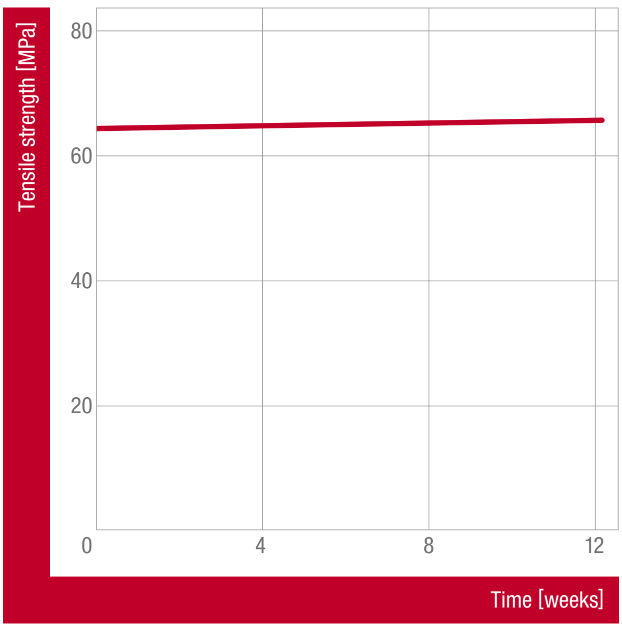


Figure 18: Exposure of Ultraform® N2320 003 to AdBlue® at 60°C [140°F].



[2] Gerhard W. Becker, Dietrich Braun, Ludwig Bottenbruch, Rudolf Binsack, Kunststoff Handbuch [Plastics Manual] Volume 3/4, Technische Thermoplaste-Polyamide [Engineering Thermoplastic Polyamides], page 246, published by Carl Hanser Verlag, 1998.

[3] Wolfgang Sauerer, Tilman Reiner, Materialien für saubere Dieselmotoren [Materials for Clean Diesel Engines], Kunststoffe [Plastics] 3/2007, published by Carl Hanser Verlag.

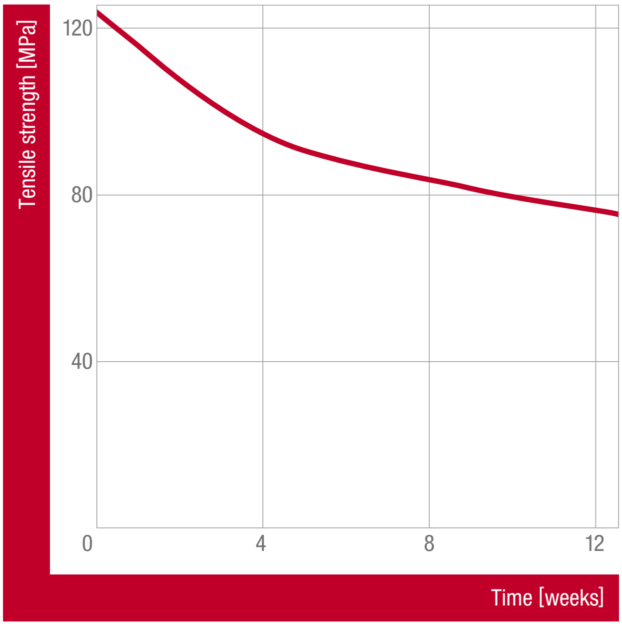


Figure 19: Exposure of Ultraform® N2200 G53 to AdBlue® at 60 °C [140 °F].

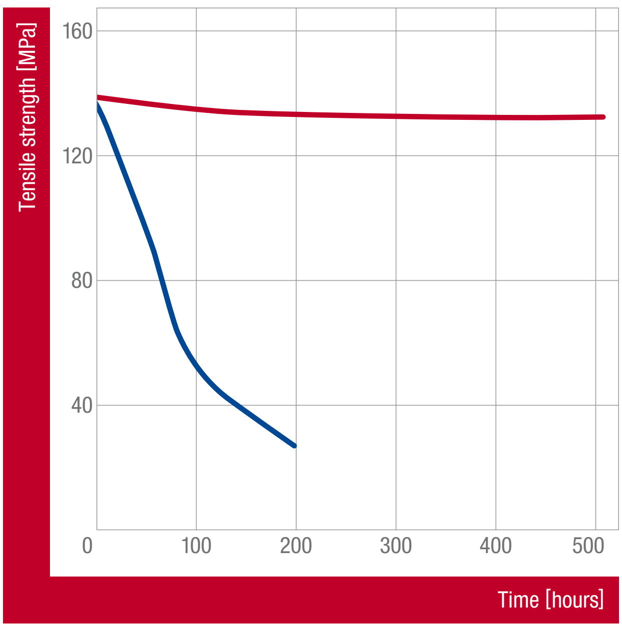


Figure 20: Exposure of Ultradur® B4300 G6 to sodium hydroxide solution of different concentrations at 23 °C [73.4 °F].
red: 4 ppm of NaOH, slightly to moderately alkaline, pH 10
blue: 10 % NaOH, highly alkaline, pH 14

Ethylene glycol

Ethylene glycol, also called shortly glycol, is known especially as an anti-freezing agent. For this purpose, it is admixed to the cooling water in automobiles (normally at a mixing ratio of 50:50). On the one hand, this accounts for anti-freezing properties down to about -40 °C [-40 °F] and, on the other hand, the vapor pressure of the mixture is lower than that of water, so that coolant temperatures above 100 °C [212 °F] at a slight overpressure are possible.

Resistance in contact with coolant

The typical temperature in the cooling systems of internal-combustion engines in automobiles ranges from 85 °C to 90 °C [185 °F to 194 °F], with peak values of up to 115 °C [239 °F]. Typical test specifications of the automotive industry are scenarios involving a coolant flow at 2 bar of overpressure and at temperatures of 135 °C [275 °F] for 1,500 hours. These conditions are simulated in laboratory tests by examining tensile bars after 1,000 hours to 3,000 hours of exposure at 120°C to 135°C [248 °F to 275 °F]. In this context, it must be pointed out that the stress differs greatly from that found in actual practice (for example, complete versus one-sided wetting with coolant, constant versus cyclically fluctuating temperatures).

Long-term media resistance of Ul

When polyamide comes into contact with glycol-water mixtures, it swells markedly. The swelling causes it to soften already after a brief contact (1 to 2 days). After that, the polymer chains begin to degrade, which is highly dependent on the temperature, as is schematically shown in Figure 21. This fundamental behavior takes place in contact with all commercially available coolants, whereas the glycol types used have to be checked individually at the prescribed mixing ratio with water.

Under the conditions in vehicle cooling systems, commercially available Ultramid® B is classified as not being sufficiently resistant. In contrast, Ultramid® A is often used, for example, for coolant expansion tanks, radiator end caps and cooling water pipes. In these applications hydrolysis-stabilized products with the designation HR (hydrolysis-resistant) and HRX are used exclusively. Like Ultramid® A, Ultramid® T is also somewhat resistant, whereas Ultramid® S has a much better resistance, as a comparison of the products in Figure 22 shows.

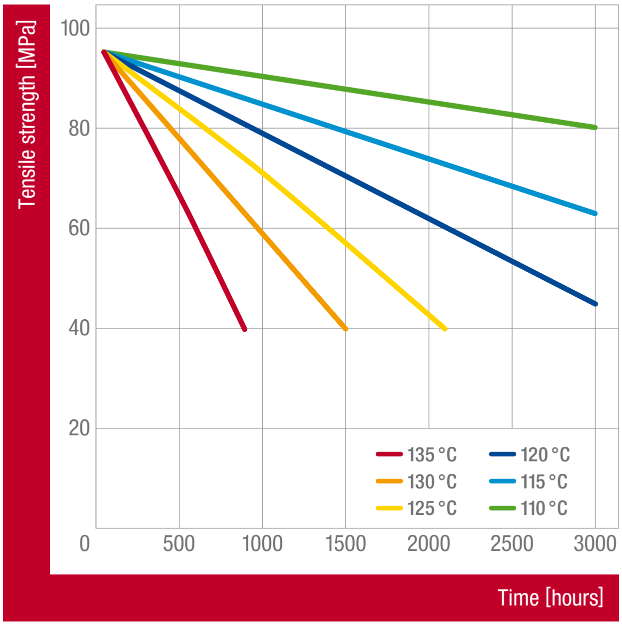


Figure 21: Resistance of Ultramid® A containing 30 % glass fibers to a coolant consisting of glycol and water, as a function of the exposure temperature (schematically): rapid softening due to swelling, marked loss of residual strength at exposure temperatures > 120 °C [> 248 °F]. For comparison purposes: the tensile strength is 190 MPa when dry, 120 MPa at 1.7 % moisture, 95 MPa at 5.5 % moisture.

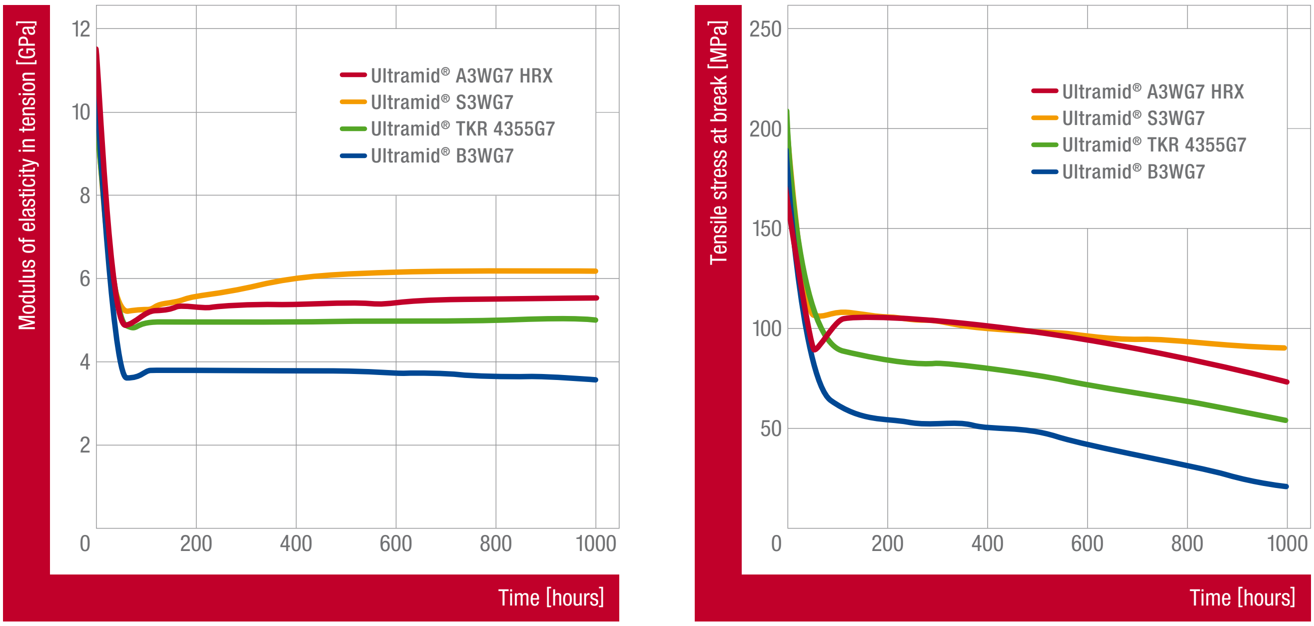


Figure 22: Comparison of the resistance of Ultramid® A, B, S and T to coolants during exposure to Glysantin® G48/water (50:50 mixing ratio) at 130 °C [266 °F].

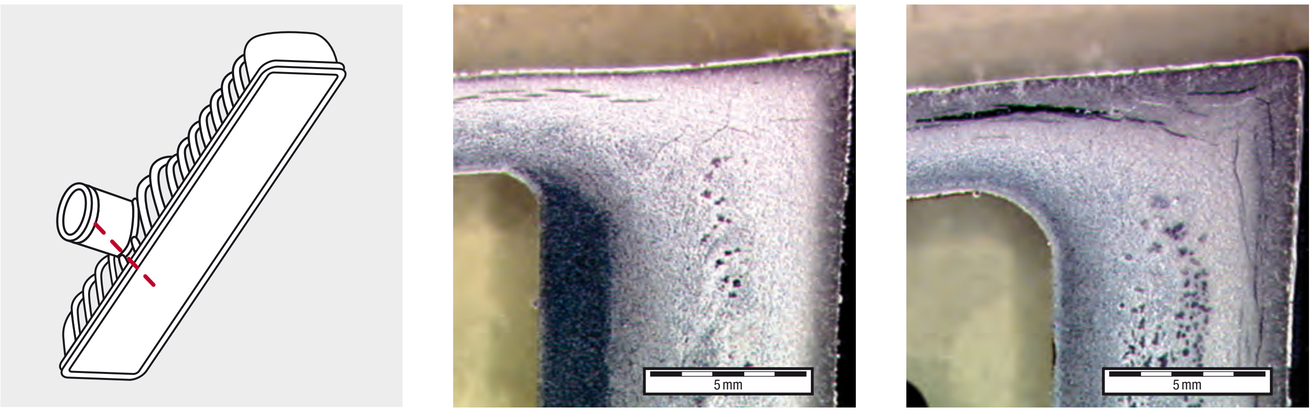


Figure 23: Section through the connection piece of a radiator end cap following a service-life test; middle: Ultramid® A3WG6 HRX; right: standard PA66 GF30 HR, clearly visible material damage in the form of cracks which have not led to component failure.

Aged components sometimes show cracks caused by contact with coolants, as illustrated in Figure 23 for sections of radiator end caps. This is why it is common practice to design the components with a sufficiently thick wall of about 3 mm, in order to take into account the reduced residual strength.

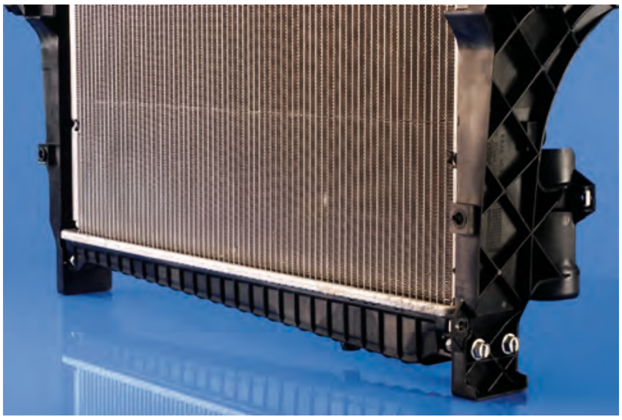


Figure 24: End caps of vehicle radiators are a typical application for hydrolysis-resistant PA66 types such as Ultramid® A3HG6 HR.

Glycol is likewise sometimes used as a heat-conducting medium in solar thermal energy systems. Commercially available Ultramid® is not a suitable material for pressurized systems operating at temperatures of up to 200 °C [392 °F]. In contrast, when it comes to drain-back systems with typical temperatures below 90 °C [194 °F], Ultramid® can be considered to be resistant to a limited extent, depending on the requirements made of the dimensional stability.

Ultraform® can only be used to a limited extent for applications in the cooling system of an internal-combustion engine in an automobile; temperature peaks above 110 °C [230 °F] must be avoided.

Long-term media resistance of Ul

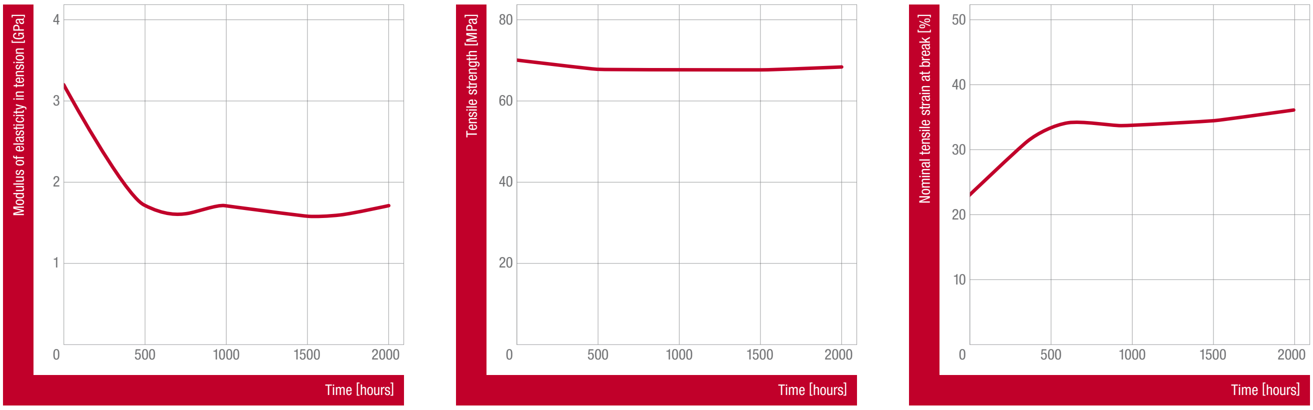


Figure 25: Exposure of Ultraform® S1320 003 to Hydraulan® 408 at 120 °C [248 °F].

Resistance to contact with brake fluids and hydraulic fluids

Derivatives of ethylene glycol, for instance, higher homologues (such as diethylene glycol, triethylene glycol) and its ethers (e.g. triethylene glycol monobutyl ether) are used in conventional brake fluids as well as in special hydraulic fluids.

Ultraform® and Ultramid® are generally resistant to brake and hydraulic fluids containing glycol derivatives. Figure 25 shows the example of exposure of Ultraform® S1320 003 to Hydraulan® 408 brake fluid at 120 °C [248 °F]. In the equilibrium state, the material absorbs approximately 4.5 % of the medium. Consequently, Hydraulan® 408 has a pronounced softening effect on Ultraform® S1320 003. The tensile strength and the nominal tensile strain at break, however, remain at a constant high level after swelling.

Figure 26 shows the data for Ultramid® A3HG5 and Ultramid® A3HG7 in DOT 4 brake and hydraulic fluid under typical conditions that are used to simulate the service life of a vehicle. Since brake fluid is hygroscopic[4], water is added to the test fluid, which causes the polyamide to swell.

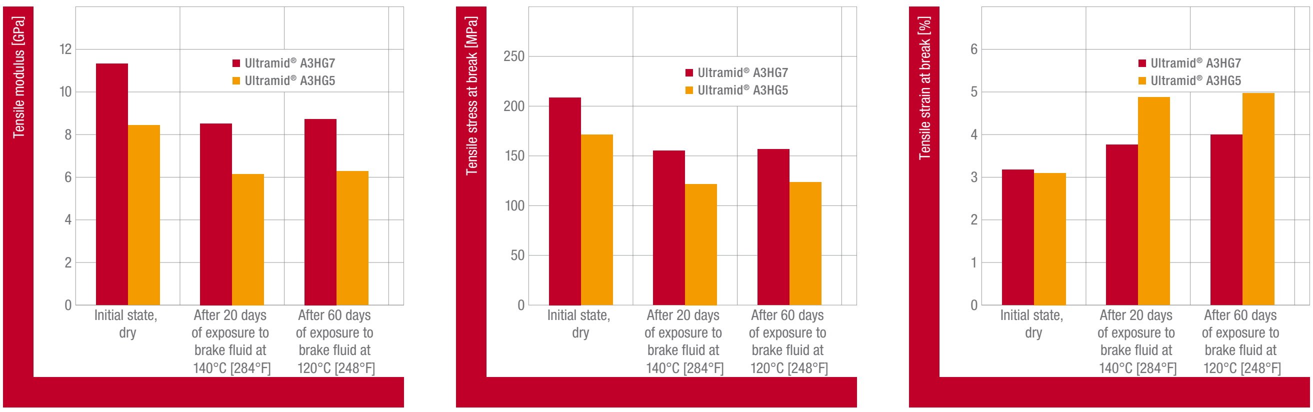


Figure 26: Exposure of Ultramid® A3HG5 and Ultramid® A3HG7 to ATE Super DOT 4 brake and hydraulic fluid plus 3 % water.

[4] hygroscopic: absorbs moisture from the air and binds it

Esters

Esters constitute a group of organic compounds that are formed by the reaction of an alcohol and an oxoacid, while splitting off water. Esters on the basis of organic acids must be distinguished from esters on the basis of inorganic acids. The former include, for instance, the carboxylic acid esters. They have the following common structural element: R-COO-R'. They are widespread in nature in the form of greases, oils and even fragrances.

As a rule, the engineering plastics Ultraform®, Ultramid® and Ultradur® provide good resistance to greases (e.g. edible fats, lubricant greases), oils (e.g. cooking oils, lubricants, motor oils) and surfactants based on carboxylic acid esters. An elevated content of free acids has to be seen as being critical since this accelerates the splitting of the polymer chains. This is particularly true of esters based on inorganic acids. If the esters are hydrolytic[5] or thermally unstable, and the ongoing degradation during the utilization phase releases acid continuously, it is recommended that the resistance of these engineering plastics is tested by means of experiments.

The engineering plastics Ultraform®, Ultramid® and Ultradur® can come into contact with fatty-acid methyl esters in components that carry fuel. Fatty-acid methyl esters constitute the main ingredient of biodiesel. In Europe, this product is usually obtained through transesterification of rapeseed oil with methanol. In the United States, the vegetable oil base is usually soybean oil.

Aside from pure biodiesel (B100), biodiesel fuel is normally used admixed to mineral-oil-based diesel. Depending on the content of biodiesel, a distinction is made, for instance, between B20 (20 % parts by volume of biodiesel), B30 or B50.

[5] hydrolytic: splits chemical compounds through reaction with water

Long-term media resistance of Ul

Ultraform® S1320 0021, which is highly stabilized against hot diesel, shows outstanding resistance to pure biodiesel (B100 according to DIN EN 14214). At an exposure temperature of 140 °C [284 °F], no drop in the strength and yield strain properties is observed after 200 days. At a temperature of 140°C [284°F], the product only absorbs 1% of biodiesel. The modulus of elasticity here decreases from about 3.0 GPa to 2.4 GPa.

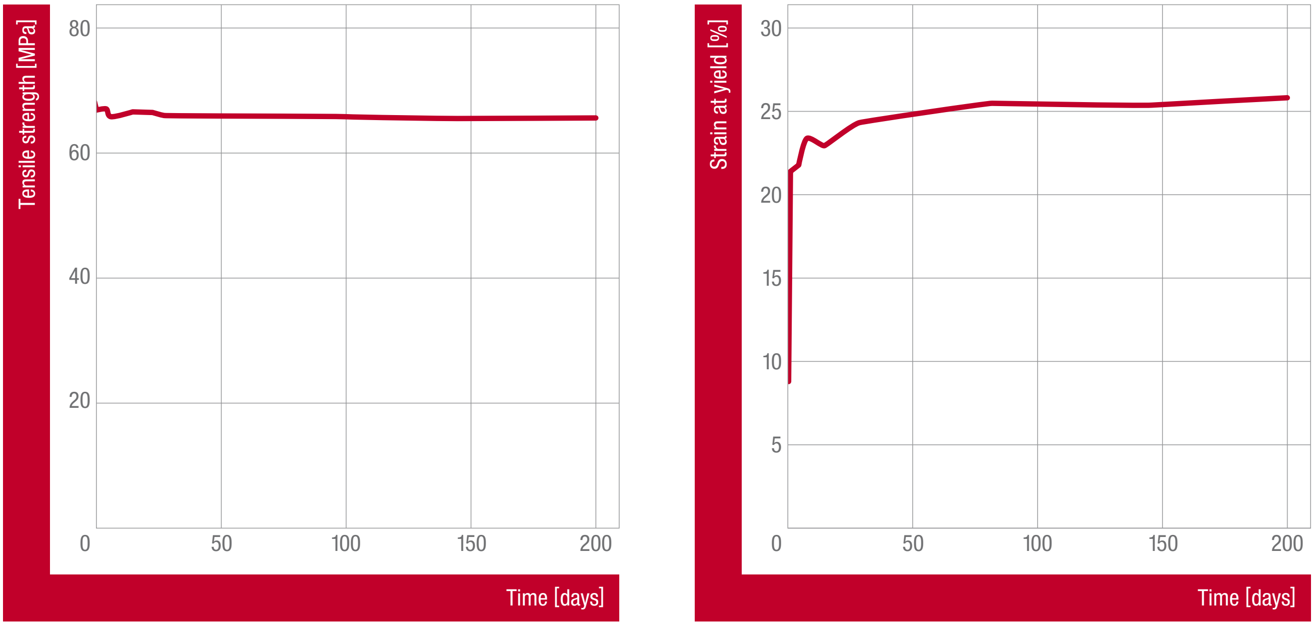


Figure 27: Exposure of Ultraform® S1320 0021 to biodiesel (B100 according to DIN EN 14214) at 140 °C [284 °F].

Commercially available Ultramid® is only resistant to biodiesel to a limited extent. Moreover, its resistance is highly dependent on the origin and composition of the biodiesel. The resistance in pure rapeseed methyl ester (RME) is good; see Figure 28. The resistance to biodiesel made on a different basis can be considerably worse. Since the composition of biodiesel is not standardized, each type has to be tested individually, especially those from exotic sources.

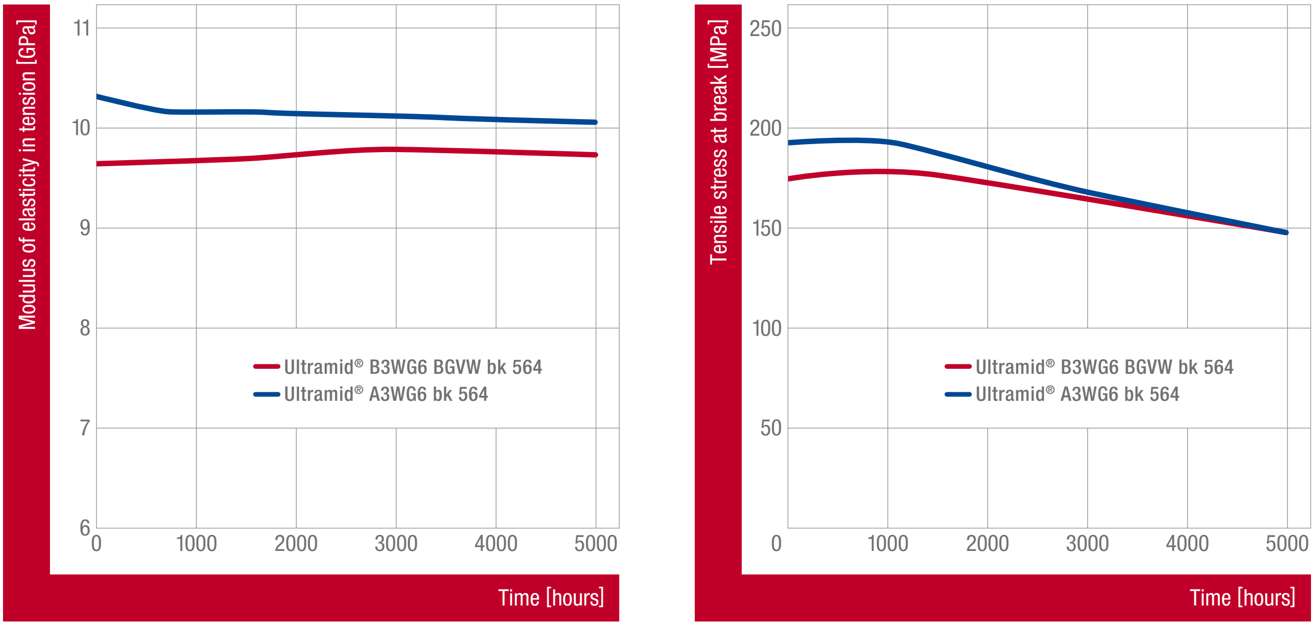


Figure 28: Resistance of Ultramid® A and B to biodiesel (100% RME) at 140 °C [284 °F].

Long-term media resistance of Ul

Aliphatic alcohols

Aliphatic alcohols (alkanols) are primarily linear aliphatic hydrocarbons having one or more OH groups.

Due to their polar properties and small molecule size, short-chain aliphatic alcohols (for instance, methanol, ethanol) are absorbed by polyamides into the amorphous areas. This causes a change in volume and a reduction in stiffness and strength, since small molecules such as those of water or alkanols have a softening effect on polyamides.

This effect is more pronounced in Ultramid® B than in the higher crystalline Ultramid® A or in the partially aromatic Ultramid® T.

Important applications where polyamides come into contact with alcohols are the fuel systems of cars since alcohols are added to numerous types of fuel, and also components that come into contact with food products containing alcohol.

Fuels and their chemical composition:

Methanol and ethanol are used either in pure form (Brazil: M100, E100) or as a component of conventional fuels. Special bioethanol has become considerably more significant in recent years. Its percentage in the fuel fluctuates regionally and is usually between 5% or 10% (Europe: E5 or E10) and 100% (Brazil: E100).

The mixtures based on Otto fuels are designated in accordance with the percentage of alcohol they contain. M15 or E15 are, for instance, fuels containing 15% by volume of methanol or ethanol. Moreover, for testing purposes, a wide array of well-defined test fluids are employed so that the test results can be compared. The nomenclature for the unambiguous designation of test fuels and their specific compositions are described extensively in SAE standard J1681.

Figure 29: Quick connectors for fuel lines using Ultramid® T.

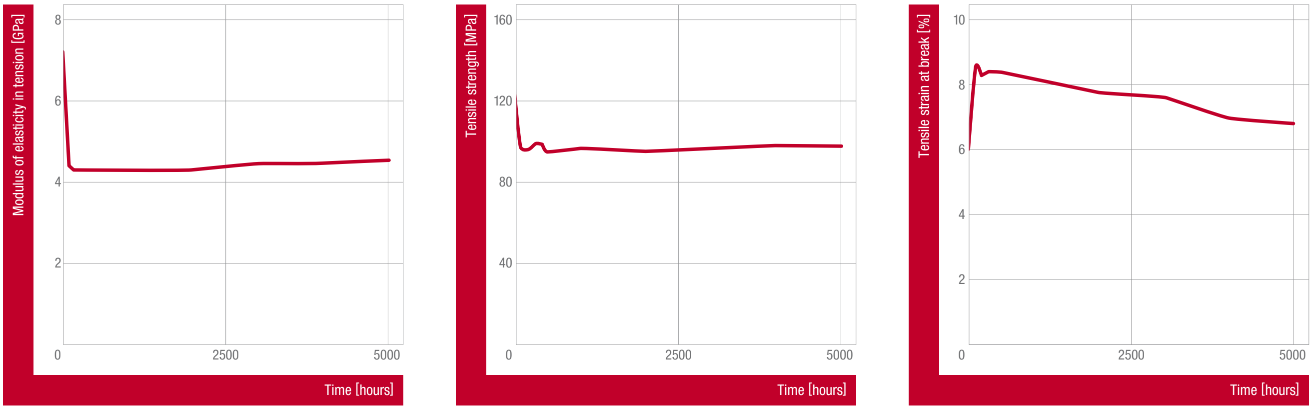


Figure 30: Exposure of Ultramid® A3WG6 HRX bk 23591 to E50 at 90 °C [194 °F] (zero value = quickly conditioned according to ISO 1110).

Ultramid® A3WG6 HRX bk 23591 shows good resistance to E50[6] at 90°C [194°F] for up to 5,000 hours (Figure 30). In its state of equilibrium, this material absorbs approximately 4.5 % of E50.

Ultraform® is very well-suited for use in contact with fuels containing alcohol. This is the reason why it has been used in tank modules (Figure 9) for many years.

Figure 31 shows by way of an example the exposure of Ultraform® S1320 003 to CM15A[7] at 60°C [140°F]. As a result of swelling with about 3.5 % of CM15A, the modulus of elasticity drops from 3.0 GPa to approximately 1.8 GPa. The modulus of elasticity, the tensile strength and the yield strain then stay at constant levels for up to about 2,000 hours.

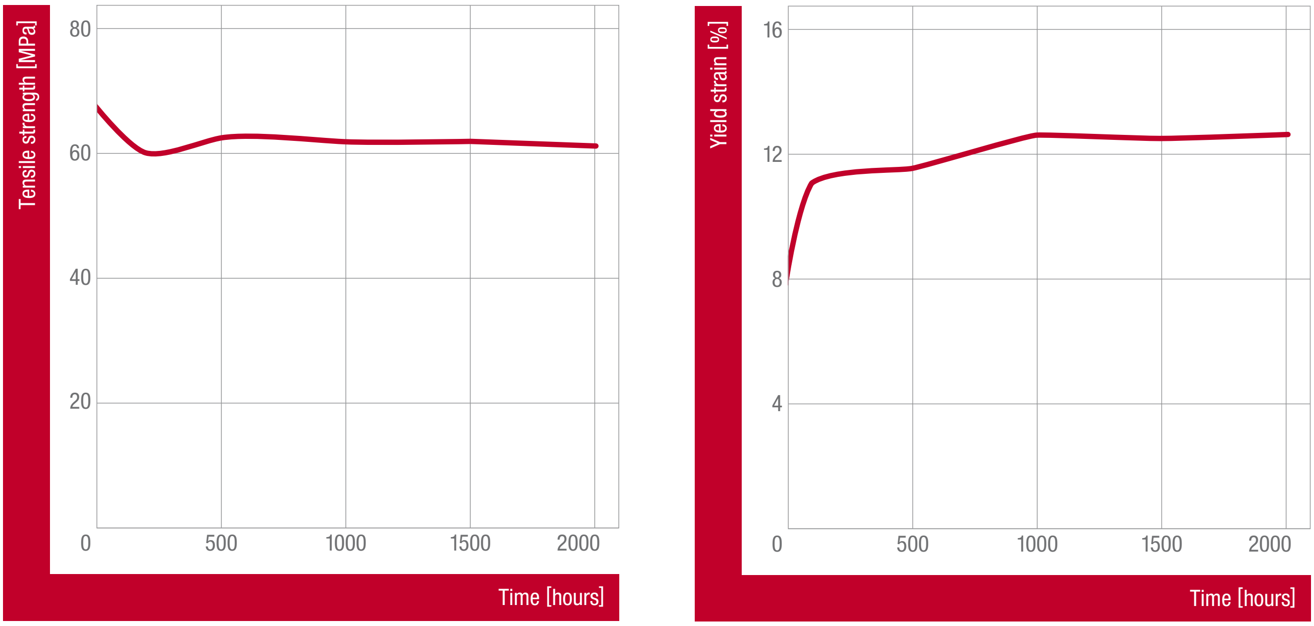


Figure 31: Exposure of Ultraform® S1320 003 to CM15A at 60°C [140°F].

[6] E50: 50 % bioethanol and 50 % 98-octane premium gasoline.
[7] CM15A: 42.5 % toluene, 42.5 % isooctane, 15 % methanol with aggressive additives.

Long-term media resistance of Ul

In CE85A[8] at 65 °C [149 °F], Ultraform® S1320 003 absorbs approximately 2.7 % of the medium. After the equilibrium has been established, the modulus of elasticity, the tensile strength and the yield strain then stay at constant high levels (Figure 32).

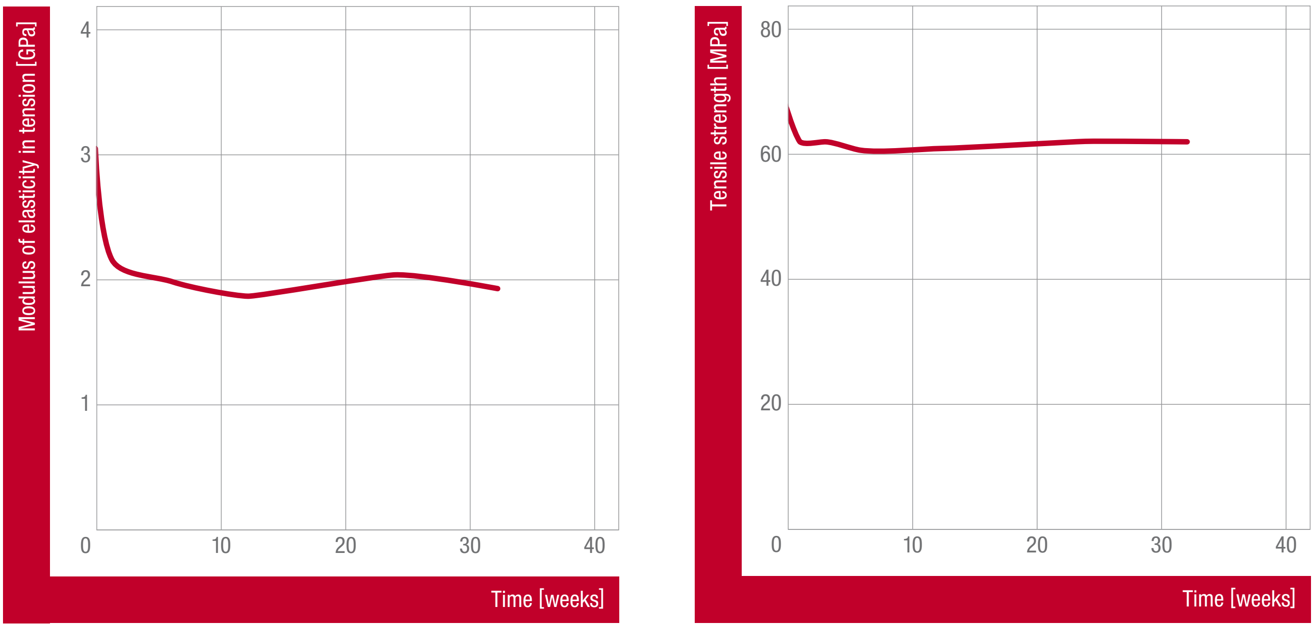


Figure 32: Exposure of Ultraform® S1320 003 to CE85A at 65 °C [149 °F].

Ultradur® is somewhat resistant to aliphatic alcohols as a component of fuels. Particularly in the case of prolonged contact at high temperatures, it has to be assumed that the fuel components containing alcohol will cause a degradation of the polymer chains. Figures 33 and 34 show the behavior of a glass-fiber reinforced Ultradur® in contact with test fuels containing alcohol. The low-alcohol fluids (CM5[9], CE10[10]) have a high toluene content; the high-alcohol fluids (CM85A[11], CE85A[12]), in contrast, have a low toluene content. Above the glass-transition temperature of about 60 °C [140 °F], Ultradur® swells considerably more markedly due to toluene than it does due to methanol or ethanol. Owing to this difference in the swelling, the stiffness and strength of the material drop more due to contact with the (low-alcohol) fluids that have a high toluene content. The irreversible material damage due to polymer degradation, however, tends to occur more in fluids that have a high alcohol content. This can be seen in Figure 33 on the basis of the decrease in the tensile stress at break from 750 to 1,000 hours (blue curve).

[8] CE85A: 85 % ethanol with aggressive additives, 7.5 % isooctane and 7.5 % toluene.
[9] CM5: 5 % methanol, 47.5 % isooctane and 47.5 % toluene.
[10] CE10: 10 % ethanol, 45 % isooctane and 45 % toluene.
[11] CM85A: 85 % methanol with aggressive additives, 7.5 % isooctane and 7.5 % toluene.
[12] CE85A: 85 % ethanol with aggressive additives, 7.5 % isooctane and 7.5 % toluene.

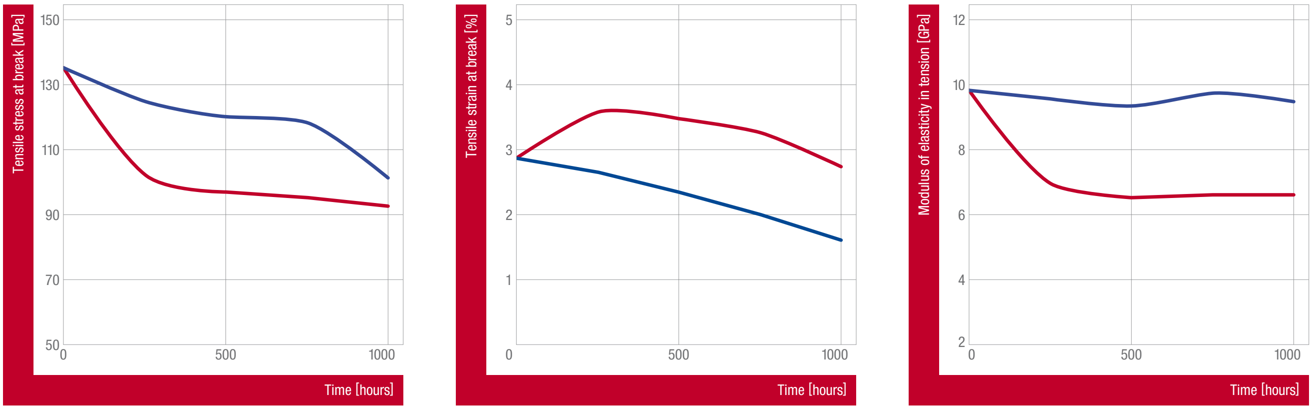


Figure 33: Exposure of Ultradur® B4300 G6 bk Q16 15007 to fuels containing methanol.
red: CM5[9] at 90 °C [194 °F]
blue: CM85A[11] at 90 °C [194 °F]

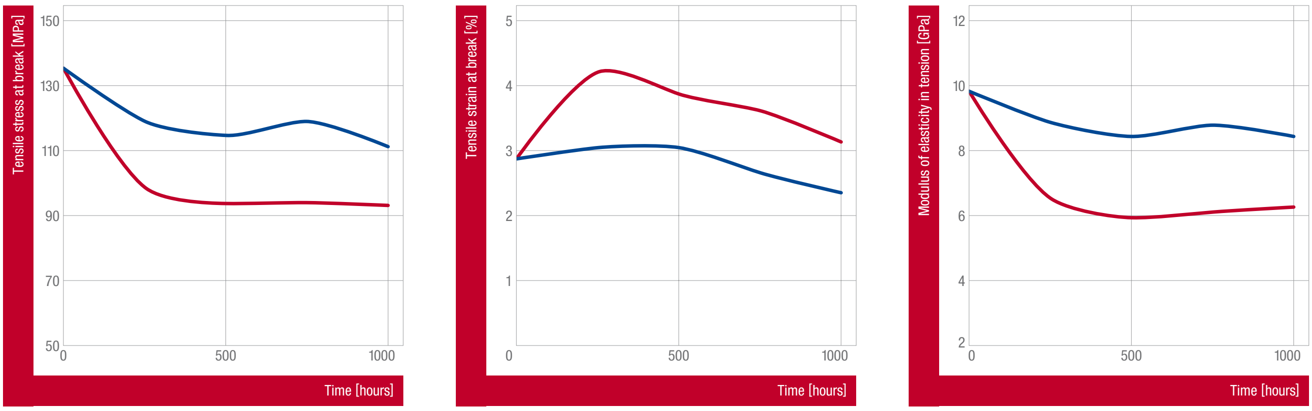


Figure 34: Exposure of Ultradur® B4300 G6 bk Q16 15007 to fuels containing ethanol.
red: CE10[10] at 90 °C [194 °F]
blue: CE85A[12] at 90 °C [194 °F]

Long-term media resistance of Ul

Water and aqueous solutions

Water

The general influence of water on Ultramid® in the form of swelling has been described in a number of passages of this publication. Details can also be found in the Ultramid® brochure and in the brochure about the conditioning of finished parts made of Ultramid®. When water swells polyamide, this lowers the glass-transition temperature. Since the material softens at temperatures above the glass-transition point, the mechanical properties change as follows: the modulus and the strength decrease, while the toughness increases. Figure 35 shows this effect by way of an example for unreinforced and glass-fiber reinforced Ultramid® A. As the water content in the polymer increases, the tensile modulus above the corresponding glass-transition temperature is reduced.

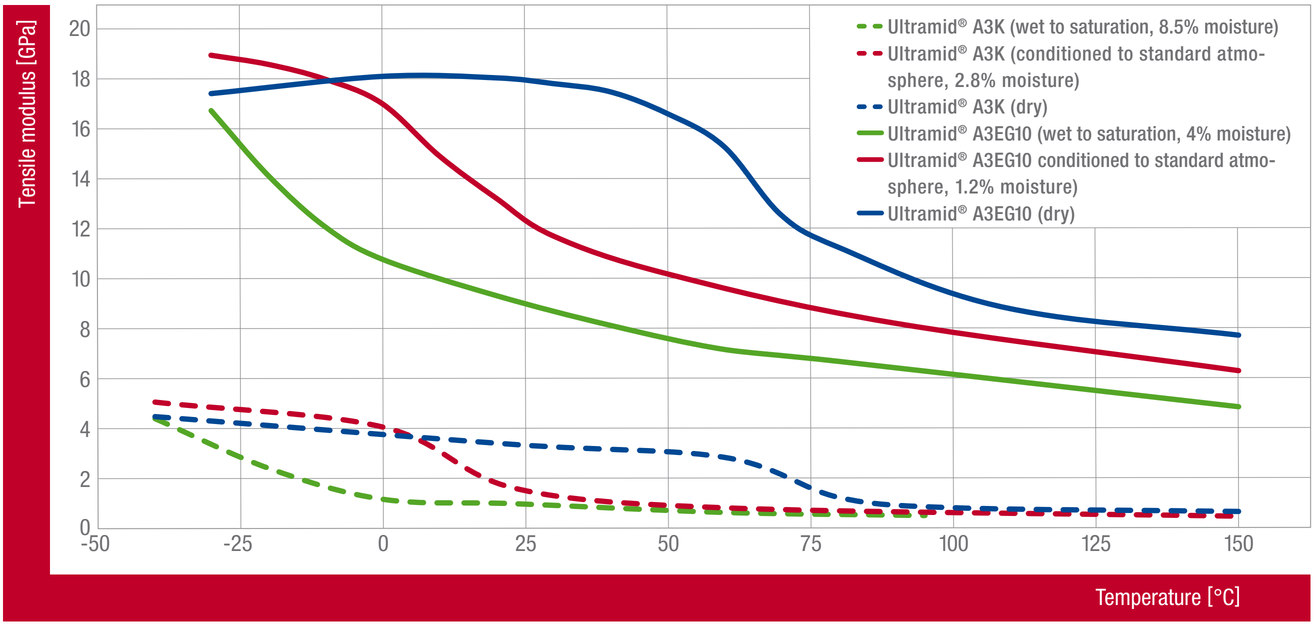
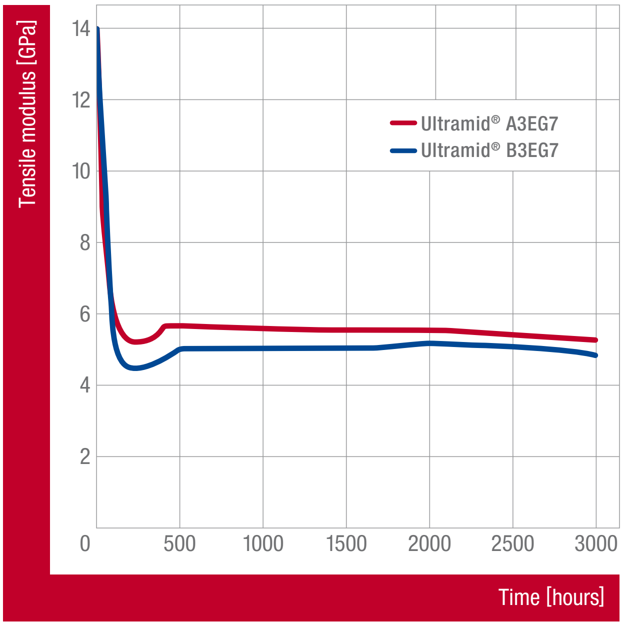


Figure 35: Tensile modulus of Ultramid® A3K and A3EG10 as a function of the temperature and moisture.

Equilibrium moisture is established depending on the ambient conditions (in humid air or under water, at different temperatures). If, after this moisture level has been reached, the mechanical properties no longer change, as shown in Figure 36, there is no hydrolytic degradation, but only swelling. At very high temperatures, however, water causes severe hydrolytic degradation in Ultramid®: for instance, if the material has not been sufficiently dried before being injection molded, the processing temperatures of about 280 °C [536 °F] cause cracking of the molecule chains.



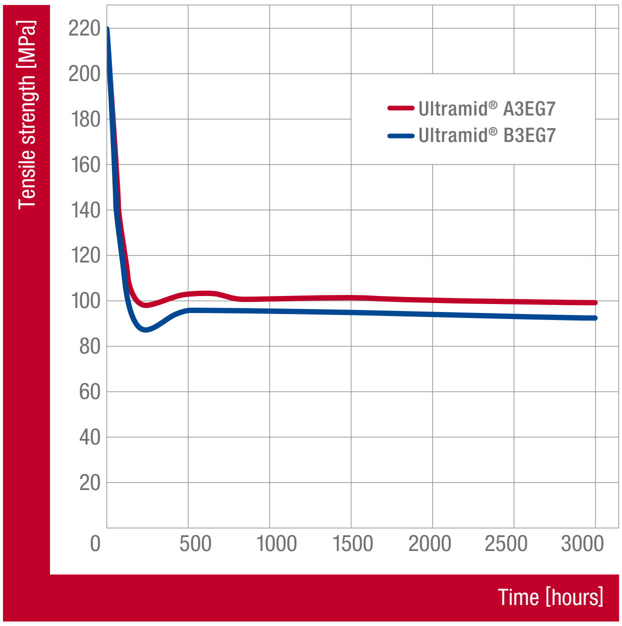


Figure 36: Exposure of Ultramid® A3EG7 and B3EG7 to demineralized water at 65 °C [149 °F], with the water being replaced on a weekly basis.

Long-term media resistance of Ul

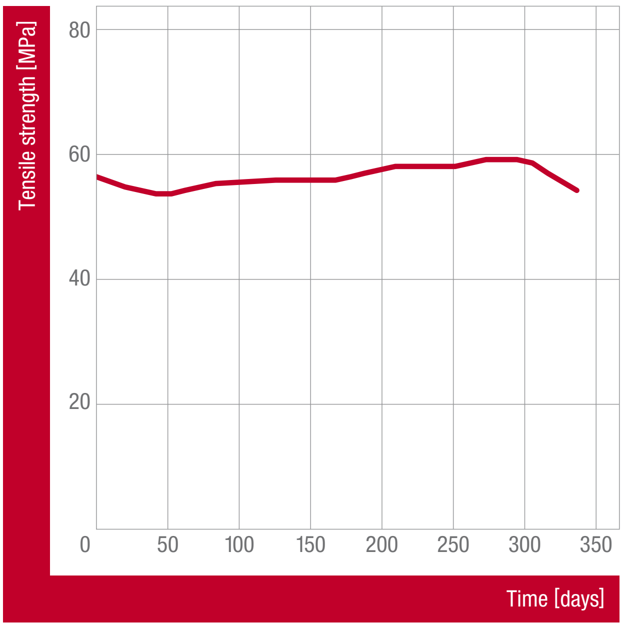
The hydrolytic aging of Ultradur® depends on several factors, of which the temperature and moisture content in the component are particularly important.

Tensile test bars with a thickness of 1.6 mm (according to ASTM D638) made of Ultradur® B4520 still show a tensile strength that is practically at its initial level (Figure 37), even after being kept in water at 60 °C [140 °F] for more than 300 days. The corresponding elongation at maximum stress increases markedly at the beginning of the exposure since the yield point is shifted from about 3.5 % to about 11 % elongation as a result of the exposure. Test specimens that were exposed for longer than 250 days no longer show a yield point. The drop in the elongation at maximum stress after 250 days is associated with a change from ductile to brittle fracture behavior.

When it comes to hydrolytic aging in humid air, the relative humidity is a crucial parameter that determines the moisture content in the interior of the component. At 100 % relative humidity and under exposure to water in its liquid form, theoretically an equilibrium with the same moisture content is reached.

Figure 38 shows that test bars (1.6 mm according to ASTM D638) made of Ultradur® B4520 still have a high strength level, even after 120 days at 70 °C [158 °F] and 62 % relative humidity. Under more demanding climate conditions (85 °C [185 °F] and 85 % relative humidity), however, a drop in the tensile strength can be observed after about 30 days.

Ultradur®, which can withstand exposure to demanding conditions as 85 °C [185 °F] and 85 % relative humidity for long periods of time, is also offered by BASF in a grade with the suffix HR (= hydrolysis-resistant). Figure 39 shows a comparison between two Ultradur® grades, each with 30 %-glass fiber reinforcement. The HR grade B4330 G6 HR bk 15045 shows a somewhat lower initial strength. This value, however, stays at a high level over the course of 120 days. The comparative grade B4300 G6 bk Q16 15007, in contrast, is already clearly damaged after 40 days.



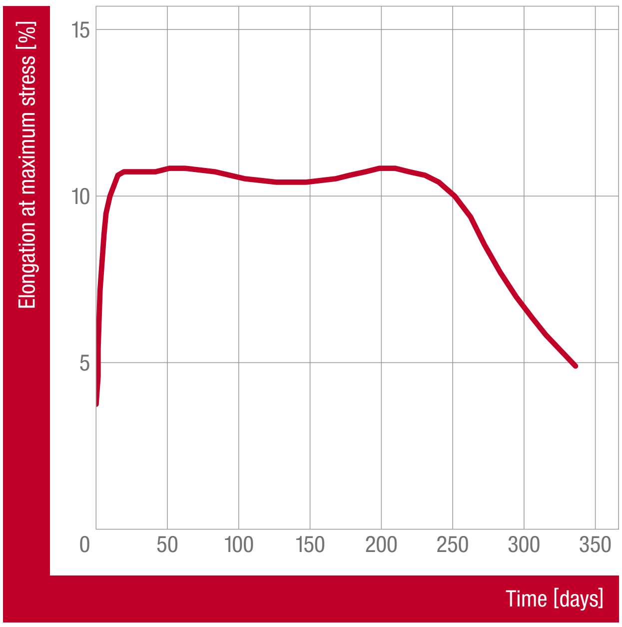


Figure 37: Exposure of Ultradur® B4520 to hot water at 60 °C [140 °F].

tramid®, Ultradur® and Ultraform®

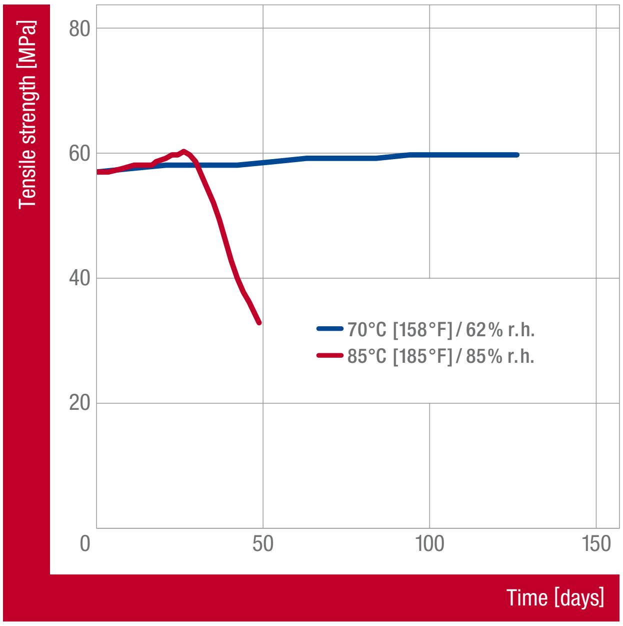


Figure 38: Tensile strength of Ultradur® B4520 under different climate conditions: 70 °C [158 °F] and 62 % relative humidity as well as 85 °C [185 °F] and 85 % relative humidity.

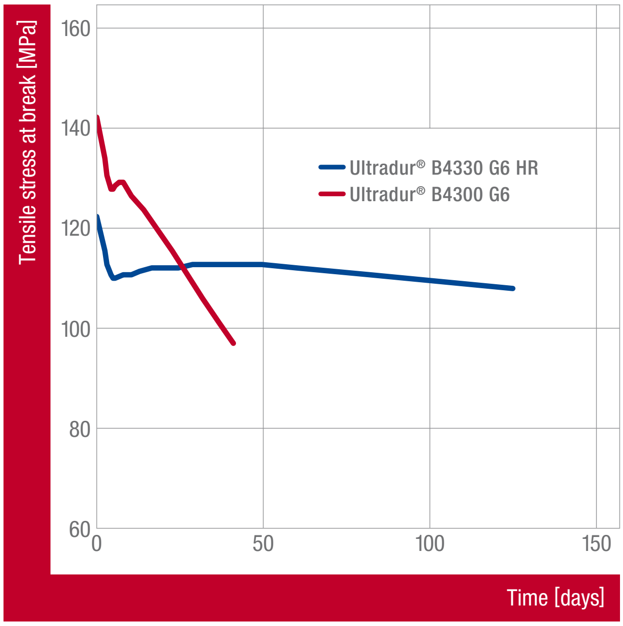


Figure 39: Tensile stress at break of hydrolysis-stabilized Ultradur® B4330 G6 HR and of non-stabilized Ultradur® B4300 G6 in a hot-moist climate (85 °C [185 °F] and 85 % relative humidity).

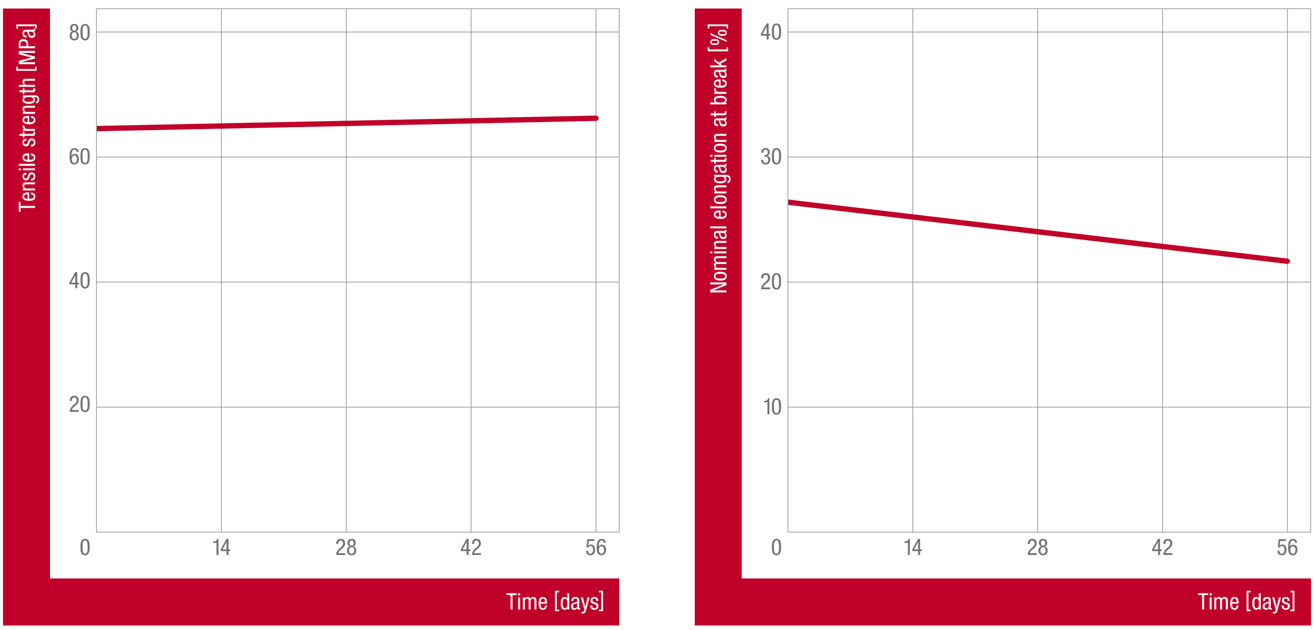


Figure 40: Exposure of Ultraform® N2320 003 to demineralized water at 100 °C [212 °F].

Unreinforced Ultraform® grades such as the injection-molding grade Ultraform® N2320 003 show an outstanding resistance to hot water. No loss in strength was found after exposure to demineralized water for 56 days at 100 °C [212 °F]. Only the nominal elongation at break drops slightly from about 26 % to about 22 %. Due to the swelling, the tensile modulus decreases from 2.7 GPa to approximately 2.3 GPa. Glass-fiber reinforced products such as Ultraform® N2200 G53 suffer a strength loss of about 50 % in the first 500 hours in hot water because the glass fibers are hydrolytically attacked.

The suitability of engineering plastics for the drinking water industry is influenced not only by the resistance of the materials but also by the various country-specific regulations. In Europe, there are no uniform test methods and evaluations for the approval of materials that come into contact with drinking water, but rather, these are regulated on a national basis (see, for instance, KTW[13] guidelines, ACS[14] listing, WRAS[15]). For this reason, each material has to be tested in accordance with the applicable approval method. In the United States, an NSF[16] listing is mandatory.

A few of the Ultramid® and Ultradur® grades are approved for contact with drinking water in certain application and temperatures ranges. Thus, for instance, glass-fiber reinforced Ultramid® A is found in the housings of water meters, sanitary installations and the brewing units of coffeemakers. Ultradur® is used in the sector of drinking water, for example, in showerheads.

Many standard grades of the Ultraform® product line are approved for drinking-water applications as well as for contact with food products. For example, unreinforced Ultraform® is found in parts of sanitary fixtures, as showerhead inserts (Figure 41) as well as in the brewing units of automatic coffeemakers (Figure 42).

Figure 41: Ultraform® as a showerhead insert.

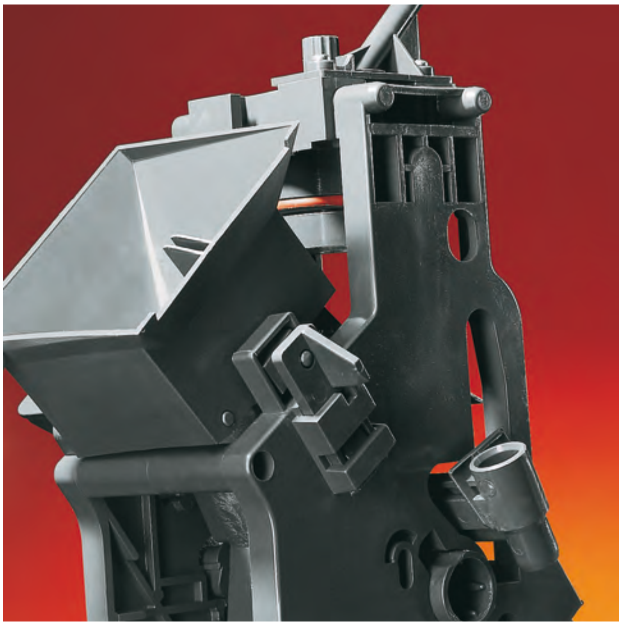


Figure 42: Ultraform® as a brewing unit of an espresso machine.

[13] KTW: Kontakt mit Trinkwasser (Germany) [German guidelines for contact with water].
[14] ACS: Attestation de Conformité Sanitaire (France) [French certification of conformity with sanitation stipulations].
[15] Water Regulations Advisory Scheme (UK).
[16] National Sanitation Foundation (USA).

Chlorinated water

Chlorine is normally added as the oxidizing chemical for purposes of disinfecting drinking water. The permissible concentration of chlorine in drinking water varies widely from one country to another. For instance, the upper limit in Germany and Austria is 0.3 ppm while it is 0.1 ppm in Switzerland. In Spain, the maximum permissible concentration is 1 ppm. In a few Asian countries and in the United States, even chlorine concentrations of up to 4 ppm are permitted.

Conventional Ultraform® is only resistant to a limited extent to chlorinated drinking water. In countries with a low content of free chlorine (<0.5 ppm) in the drinking water, Ultraform® is generally sufficiently resistant for applications in sanitary installations. Starting at a free chlorine content of 0.5 ppm to about 1 ppm, commercially available Ultraform® can no longer be used for hot-water applications, or else only with certain restrictions, if the contact time is not too long (Figure 43). For drinking water with a higher chlorine content, commercially available Ultraform® is only an option for cold-water applications involving a contact time of less than one year.

In contrast to this, Ultramid® has excellent resistance to chlorinated water. Even at chlorine concentrations that are several times higher than the concentrations normally used for disinfecting drinking water, no change in the mechanical properties is observed in comparison to exposure to non-chlorinated water.

Figure 44 shows the tensile strength of Ultramid® A3EG7 and Ultramid® B3EG6: both plastics were exposed to chlorinated water (50 ppm) in comparison to exposure to non-chlorinated water.

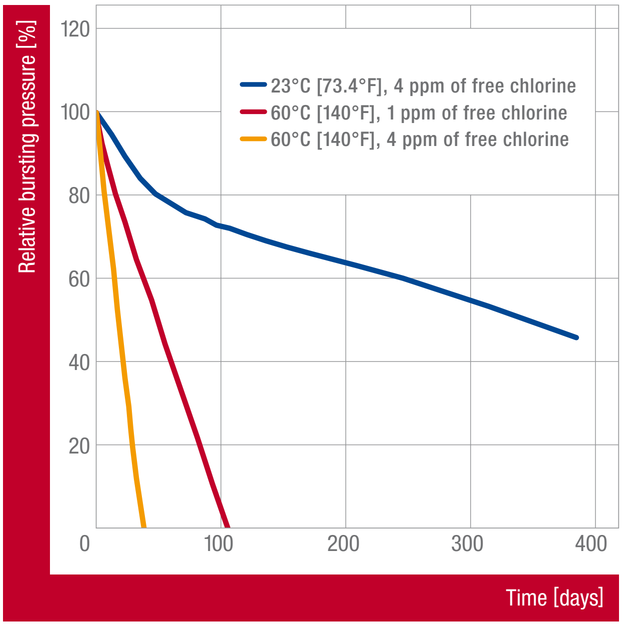


Figure 43: Resistance of Ultraform® N2320 003 to chlorinated drinking water.

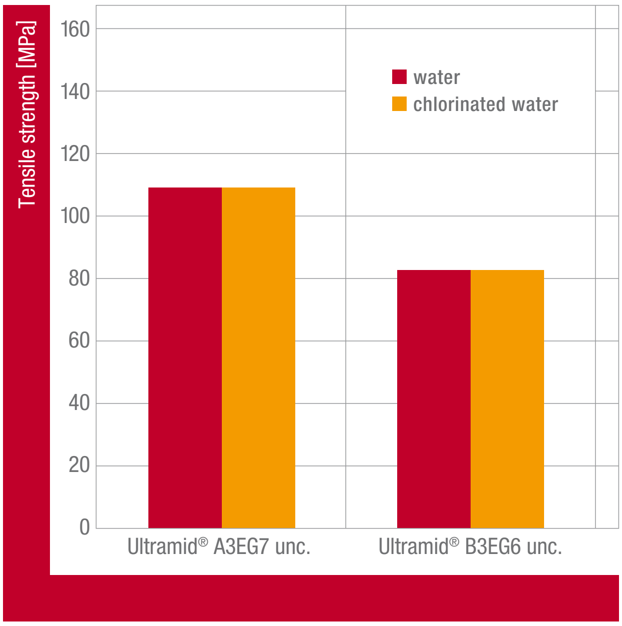


Figure 44: Tensile strength after exposure of Ultramid® A3EG7 and Ultramid® B3EG6 to chlorinated water (50 ppm) for 7 days at 65 °C [149 °F].

Aqueous salt solutions

Zinc chloride solution

Components made of Ultramid® A and B which are subjected to internal stresses or stresses when subjected to a load already have stress cracks after a brief time of contact with a zinc chloride solution. The damage can occur, for instance, when zinc-plated steel parts come into contact with solutions containing chloride (e.g. road salt).

Ultramid® S has an excellent resistance to aqueous zinc chloride solutions. For instance, Ultramid® S3WG6 bk 564 meets the requirements in terms of $ZnCl_2$ resistance as stipulated in FMVSS 106[17], as can be seen in Figure 45.

Ultramid® T is very resistant to aqueous zinc chloride solutions and it shows no susceptibility to stress cracking in this medium (Figure 46).

$ZnCl_2$ solutions do not trigger stress cracking in Ultradur®.

Commercially available Ultraform® grades are not resistant to concentrated zinc chloride solutions.

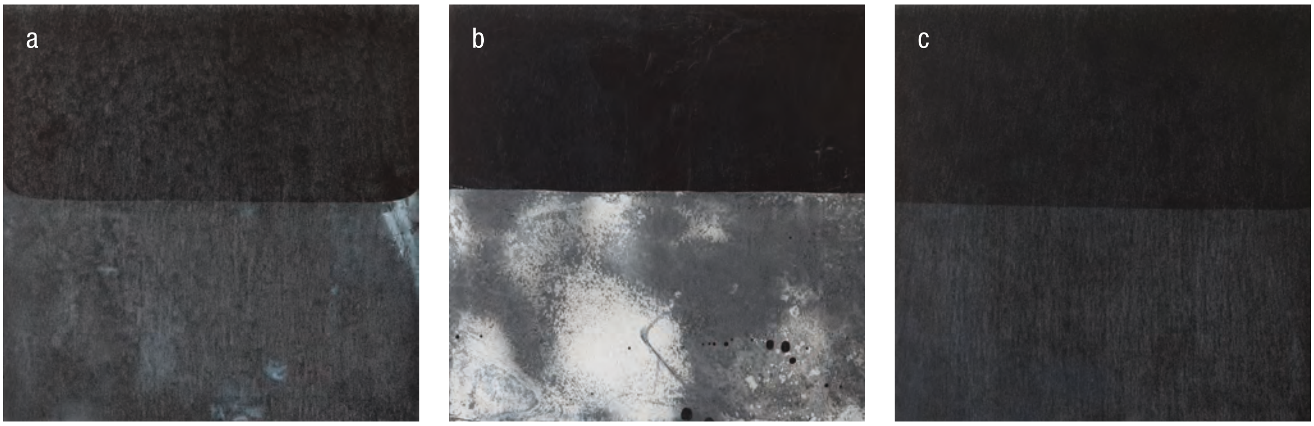


Figure 45: Surface of test plates made of Ultramid® A3WG6 HRX bk 23591 (a), Ultramid® B3WG6 bk 564 (b) and Ultramid® S3WG6 bk 564 (c) after 200 hours of exposure (half-submerged) to a 50% aqueous solution of zinc chloride at room temperature.

[17] No cracks must be visible on the surface after exposure to an aqueous 50%-solution of $ZnCl_2$ during 200 hours at 23°C [73.4°F].

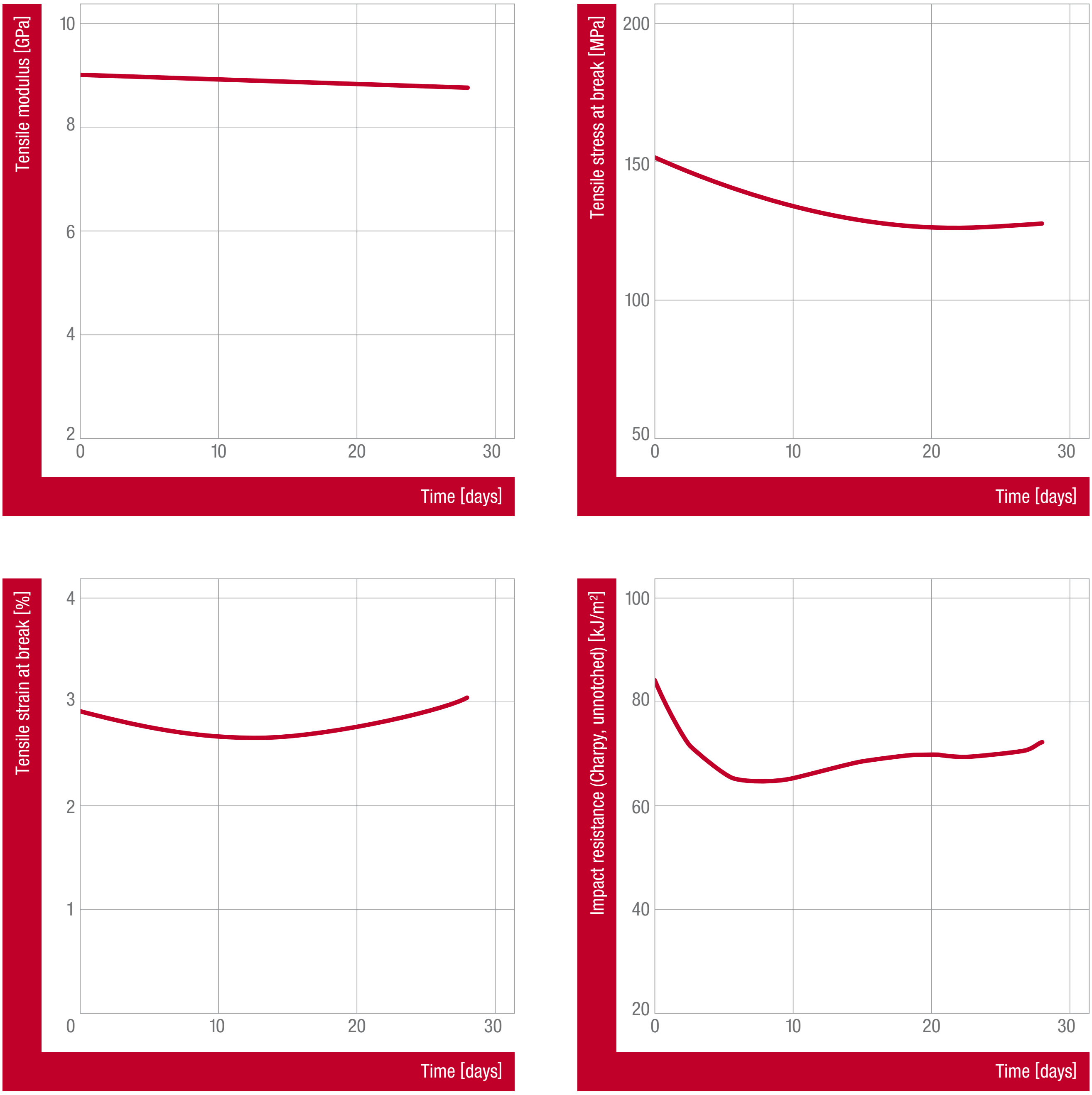


Figure 46: Exposure of Ultramid® TKR 4357G6 to a 50%-aqueous solution of zinc chloride at 60 °C [140 °F].

Long-term media resistance of Ul

Calcium chloride solutions

Calcium chloride is used as a component of road salt not only in Japan and Russia, for example, but also to an increasing extent in Central Europe. As in the case of contact with a zinc chloride solution, Ultramid® A and B are susceptible to stress cracking when exposed to calcium chloride solutions, whereas Ultramid® S, T and also Ultradur® are considerably less susceptible. The example in Figure 47 shows this on the basis of a resistance test according to an OEM standard. The test plates are exposed to a saturated calcium chloride solution in a mixture consisting of water and ethanol for 30 minutes at room temperature. They are then visually assessed. Ultramid® A and B show clear-cut changes in their surface, while the other materials do not.

Vehicle parts that can come into contact with splashing water should fundamentally be kept free of mechanical stresses.

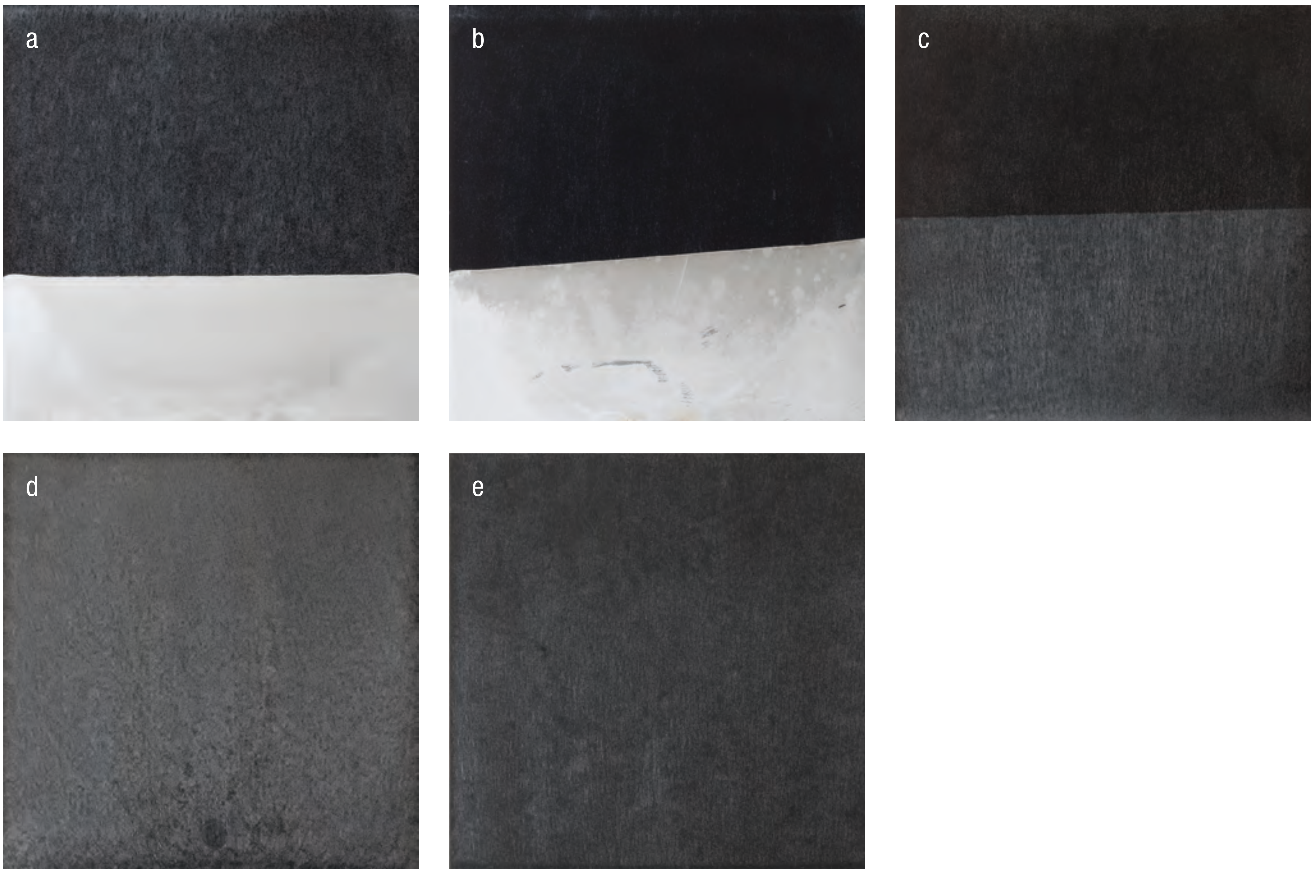


Figure 47: Surface of test plates made of Ultramid® A (a), B (b), S (c) and T (d) as well as Ultradur® (e) after being exposed (half-submerged) to a saturated calcium chloride solution for 30 minutes at room temperature.

Mineral acids

The general term "mineral acids" is used for strong inorganic acids such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3) and phosphoric acid (H_3PO_4). Mineral acids are present in strongly dissociated form in an aqueous solution, that is to say, in solution, the concentration of the acidic oxonium ions (H_3O^+) is in the same order of magnitude as the acid concentration.

At moderate temperatures, Ultramid® A and B are resistant to diluted acids. Depending on the duration of exposure, damage to the material occurs at an elevated acid concentration and at elevated temperatures.

Figures 48 and 49 show the temperature dependence of the resistance of Ultramid® to diluted acids in an example with Ultramid® B3WG6 GP. After 1,000 hours of exposure to a 0.1-molar mixture consisting of the mineral acids HCl, H_2SO_4, and HNO_3 (mixing ratio of 1:1:1, total acid concentration of 0.1 mol/l, pH value of 1) at 90 °C [194 °F], a drop in tensile strength by about 30 % was observed after re-drying. The re-drying of the test specimens allows the material damage to be examined independently of the softening effect of the swelling with water, since during exposure to diluted acid, most of the drop in tensile strength is caused by the swelling. At an elevated temperature (150 °C [302 °F]), a decrease in the tensile strength by 80 % can be already observed in the re-dried state after 180 hours in the mixture in question, and this is equivalent to a failure of the material.

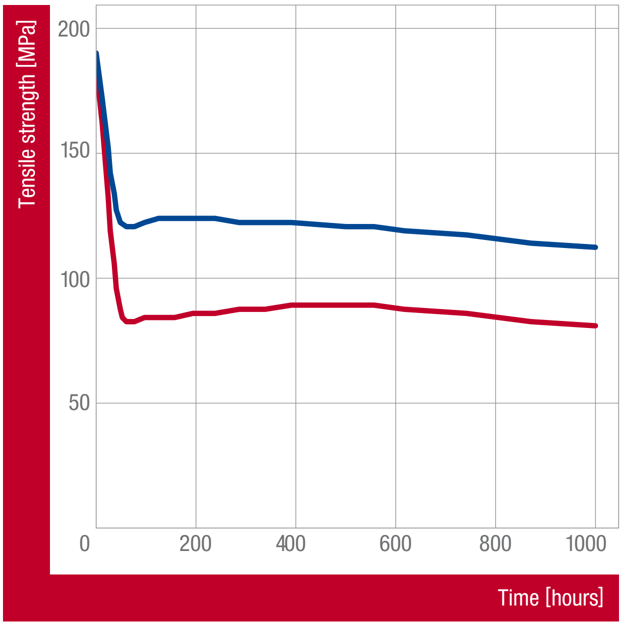


Figure 48: Tensile strength of Ultramid® B3WG6 GP bk 23210 after exposure to a mixture of HCl, H_2SO_4, and HNO_3 (pH 1) at 90 °C [194 °F].
red: testing immediately after exposure
blue: testing after re-drying

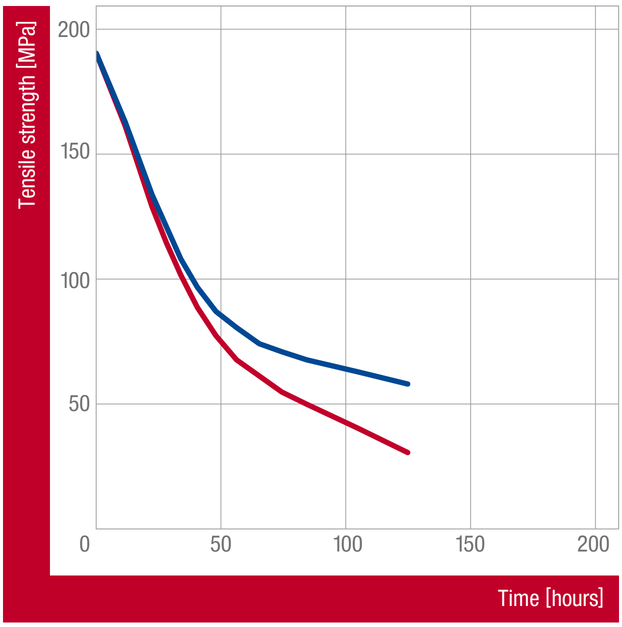


Figure 49: Tensile strength of Ultramid® B3WG6 GP bk 23210 after exposure to a mixture of HCl, H_2SO_4, and HNO_3 (pH 1) at 150 °C [302 °F].
red: testing immediately after exposure
blue: testing after re-drying

Long-term media resistance of Ul

Ultraform® is resistant to diluted mineral acids at room temperature, whereas it is considerably damaged already after a short time of exposure at an elevated temperature or in concentrated acids.

Figure 50 shows the yield stress of Ultraform® S1320 003 after exposure to a 5%-solution of sulfuric acid. No decrease is observed over a period of 40 days. In contrast to this, after exposure to a 20%-solution of sulfuric acid at 50 °C [122 °F], the tensile strength (Figure 51) already drops completely within 20 days.

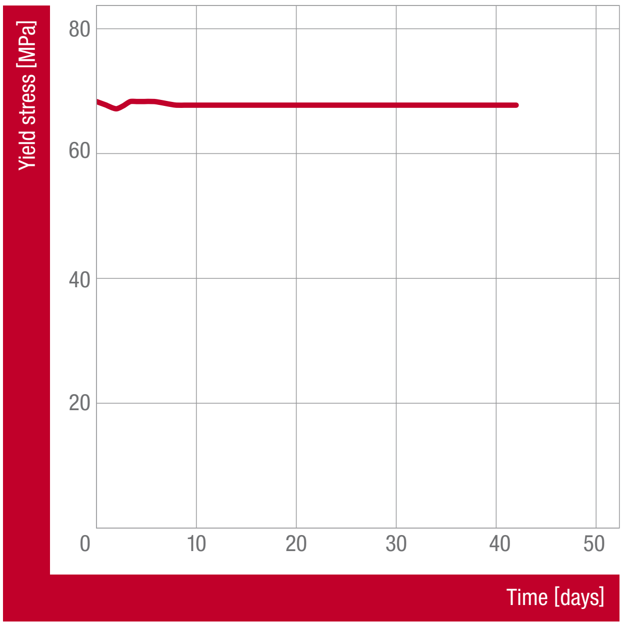


Figure 50: Yield stress of Ultraform® S1320 003 after exposure to a 5%-solution of sulfuric acid at room temperature.

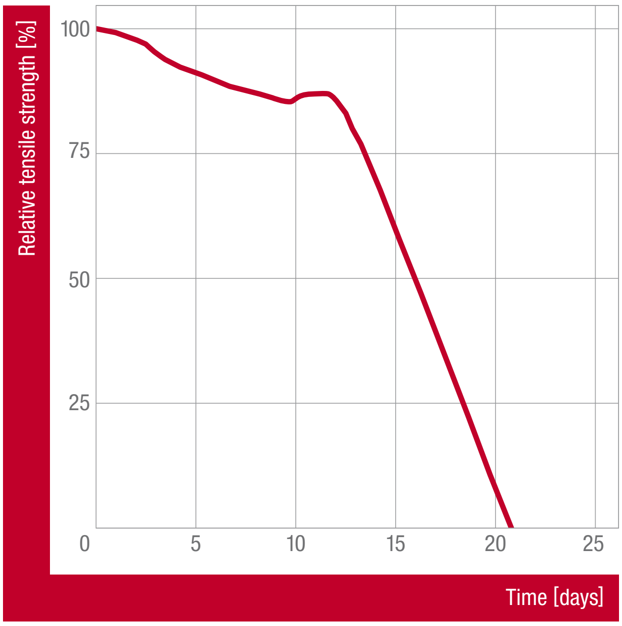
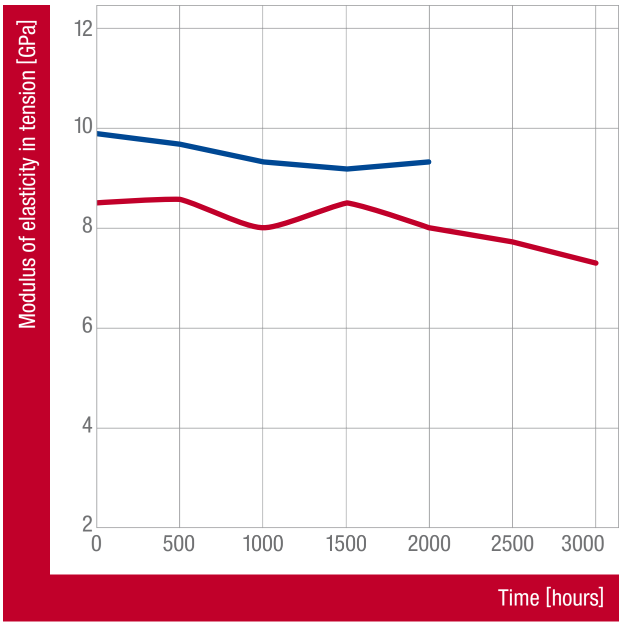


Figure 51: Relative tensile strength of Ultraform® S1320 003 after exposure to a 20%-solution of sulfuric acid at 50 °C [122 °F].

Ultradur® shows excellent resistance to diluted mineral acids at room temperature. At an elevated temperature or in contact with concentrated acids, however, considerable damage can occur already after just a brief exposure.

As an important example that is relevant for actual practice, Figure 52 shows the exposure to Ultradur® B4300 G6 and Ultradur® B4330 G6 HR to an acidic test exhaust gas. Under the given conditions, both Ultradur® B4300 G6 and Ultradur® B4330 G6 HR show an acceptable drop in tear strength. After 3,000 hours, Ultradur® B4330 G6 HR still has a tensile stress at break of 70 % of the initial value.



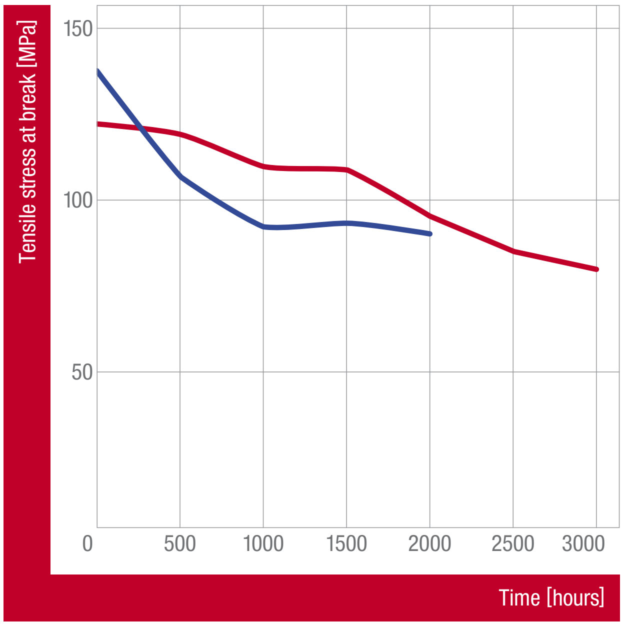
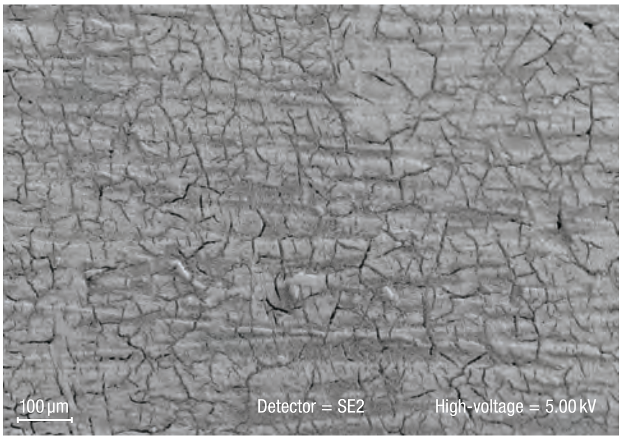


Figure 52: Exposure of Ultradur® B4300 G6 bk Q16 15007 (blue) and Ultradur® B4330 G6 HR bk 15045 (red) to an acidic test exhaust gas (5,000 ppm NO_x, 50 ppm SO_2, 10% by volume of O_2, H_2O, CO_2 each, and the rest N_2, pH value of about 1.7); the testing was conducted in test cycles of 168 hours each (24 hours at 80 °C [176 °F], 48 hours at 20 °C [68 °F], 24 hours at 80 °C [176 °F], 72 hours at 20 °C [68 °F].

Commercially available Ultraform® and Ultramid® grades are not resistant to nitrous gases and sulfur dioxide when moisture is in the air. Nevertheless, there are applications in which Ultramid® comes into contact with nitrous gases, for example, in charge air tubes and intake manifolds with exhaust-gas return. Here, although local damage occurs to the surface, this often does not lead to failure of the component because the cracks are only a few micrometers deep. In individual cases, the suitability depends on the composition of the exhaust gases and on the local geometrical conditions.

Figure 53 shows the surface of the inside of a charge air tube made of Ultramid® A3W2G6. One specimen of this component was subjected to a service-life test on an engine test stand, while another specimen was pre-damaged by thermal aging and subsequently exposed to exhaust gas condensate in a process similar to that of VDA 230-214 of the German Automotive Industry Association. On the basis of this test, it can be assumed that especially condensed exhaust gas that collects as puddles at the bottom of the component will damage the surface.



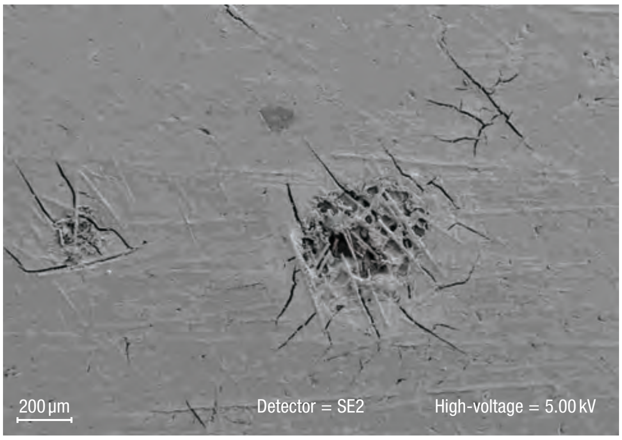


Figure 53: Surface of the inside of a charge air tube made of Ultramid® A3W2G6. On the left: after a service-life test on an engine test stand, cracks having a depth of approximately 10 µm appear. On the right: the component was aged for 2,000 hours at 140 °C [284 °F] and subsequently subjected to a corrosion test in a process similar to that of VDA 230-214. In this process, exhaust gas condensate can concentrate in individual places. In these areas, the material is visibly damaged by cracks having a depth of about 100 µm.

Organic acids

The term "organic acids" refers to those organic compounds that release protons (H^+) through dissociation, and can thus react acidically. If the solvent is water (H_2O), this causes the concentration of oxonium ions (H_3O^+) to increase significantly while the pH value decreases (pH < 7). Examples of organic compounds that fall under this general definition include the carboxylic acids (e. g. formic acid, acetic acid, citric acid, benzoic acid, etc.), sulfonic acids, phosphonic acids, phenols.

For the most part, the term organic acids is equal to carboxylic acid or a weak acid. In this section, the term organic acid will refer to a weak acid. Weak acids, unlike mineral acids (strong acids), are weakly dissociated in water and thus lower the pH value by several units less than mineral acids do. This will be shown on the basis of the following example: a 0.1-molar (mol/l) aqueous solution of acetic acid has a pH value of about 3 at room temperature; the acetic acid is present with a degree of dissociation of only about 1%; an equally concentrated hydrochloric acid, in contrast, has a pH value of about 1 (100 times more acidic) and is present with a degree of dissociation of practically 100 %.

In the solid state, weak organic acids such as, for instance, benzoic acid or citric acid are not critical for Ultramid®, Ultradur® and Ultraform®. Damage occurs at the most on the surface of the material and does not normally lead to failure of the component.

In contrast, the situation is more differentiated in terms of the resistance if the weak organic acids are present in an aqueous solution, depending on the acid concentration, on the temperature and on the duration of contact. For instance, Ultraform® S1320 003 in a 5 %-aqueous solution of formic acid at room temperature is sufficiently resistant for many applications (Figure 54).

In contrast, the same product already fails after a relatively short time in 20 %-formic acid at 50 °C [122 °F]. However, the material is resistant to a limited extent in 10 %-citric acid at 50 °C [122 °F].

Ultramid® and Ultradur® show a similarly differentiated behavior with aqueous organic acids.

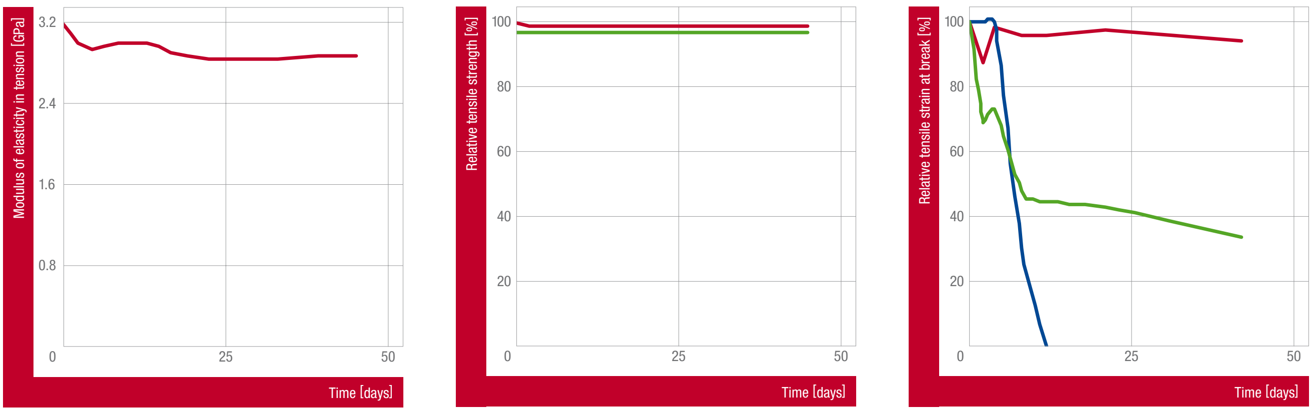


Figure 54: Exposure of Ultraform® S1320 003 to a 5 %-aqueous solution of formic acid at room temperature (red), in a 20 %-formic acid at 50 °C [122 °F] (blue), in a 10 %-citric acid at 50 °C [122 °F] (green).

Long-term media resistance of Ul

Oxidants

Generally speaking, oxidants are chemical compounds that, in chemical reactions, have a greater electron affinity than their reactants. Consequently, the bonding electrons in the reaction product are more strongly localized in the reactant stemming from the oxidant. The boundary case of a complete electron transition to the oxidant causes the formation of a salt. Whether a certain compound acts in a chemical reaction as an oxidant or as a reducing agent always depends on the relationship of the electron affinities of the two reactants. Owing to their great electron affinity, the elementary halogens (fluorine, chlorine, bromine, iodine), for example, take on the role of the oxidant in a reaction in the overwhelming majority of cases. The same applies to elementary oxygen, ozone (O_3) and peroxides such as hydrogen peroxide (H_2O_2).

Strictly speaking, oxidants are compounds that contain oxygen and that transfer oxygen to the reactant during a reaction. Typical examples of this class of substances are elemental oxygen (O_2), ozone (O_3), oxygen compounds of the halogens (for instance, hypochlorites -OCl, chlorites -OClO, chlorates $-OClO_2$, perchlorates $-OClO_3$) or other oxygen-rich compounds, for example, concentrated nitric acid, nitrates, hydrogen peroxide or potassium permanganate. Atmospheric oxygen (O_2) itself only shows a low level of reactivity under normal conditions. Gas mixtures that have a higher oxygen content than air can cause considerably faster and stronger reactions than air can. Dry salt-like oxidants (for example, sodium nitrate, potassium permanganate) can be kept at room temperature in plastic containers for a longer period of time. Contact with highly reactive liquid (e.g. elementary bromine) or gaseous (e.g. elementary chlorine) oxidants should be fundamentally avoided.

Commercially available Ultraform® grades are not resistant to oxidants such as ozone or elementary chlorine (halogens) that, in the presence of air or water, release strong acids. In this context, there is reason to assume that the degradation reaction takes place to a substantial degree via acid-catalyzed acetal splitting.

If, in contrast, the oxidation takes place under alkaline conditions, for example, using an aqueous solution of hypochlorite of sodium (soda bleaching lye), then Ultraform® is considerably more resistant. For instance, Ultraform® S1320 003 can be kept for more than 40 days in a 12.5%-aqueous solution of soda bleaching lye at room temperature without any appreciable losses in the mechanical properties (Figure 55) or in the weight of the test bars (drop $< 1\%$).

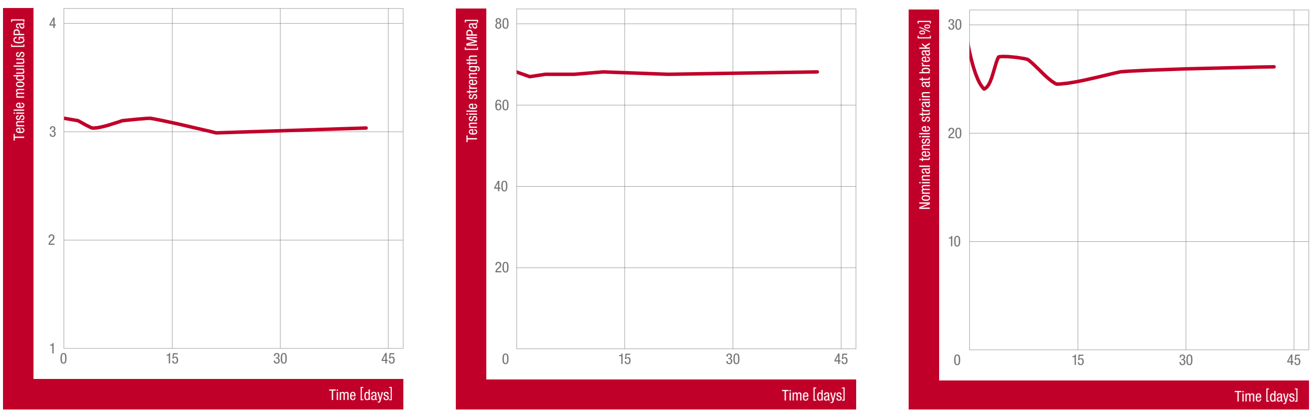


Figure 55: Exposure of Ultraform® S1320 003 to a 12.5%-aqueous solution of soda bleaching lye at room temperature.

At 50 °C [122 °F], in contrast, the test specimen measuring 80 × 10 × 4 mm shows a loss in mass of about 30 % already after 3 days.

Ultramid® TKR 4355 G7 bk 564 that was exposed to ozone (2 ppm in the air) for 72 hours at 38 °C [100.4 °F] shows a slight fading of its color (Figure 56). The mechanical properties listed in Table 3, however, are largely retained. A concentration of 2 ppm of ozone corresponds to approximately 18 times the alarm threshold value of 240 µg/m³ stipulated in the European Union.

Table 3: Properties of Ultramid® TKR 4355 GT7 bk 564.

Property	Initial value	After exposure to ozone
Tensile modulus [GPa]	11.6	11
Tensile stress at break [MPa]	195	185
Tensile strain at break [%]	2.7	2.6

Figure 56: Test specimens made of Ultramid® TKR 4355 G7 bk 564 before and after exposure to ozone. The color of the test bars faded slightly due to ozone exposure but the material properties remained largely unchanged.

Bibliography

Reference works

- Gottfried W. Ehrenstein, Sonja Pongratz, Beständigkeit von Kunststoffen [Resistance of plastics], published by Carl Hanser Verlag, 2007

- Gerhard W. Becker, Dietrich Braun, Ludwig Bottenbruch, Kunststoff Handbuch [Plastics Manual], Volume 3/1, Technische Thermoplaste – Polycarbonate, Polyacetale, Polyester, Celluloseester [Engineering thermoplastics – Polyacetals, Polyesters, Cellulose Esters], published by Carl Hanser Verlag, 1992

- Gerhard W. Becker, Dietrich Braun, Ludwig Bottenbruch, Rudolf Binsack, Kunststoff Handbuch [Plastics Manual], Volume 3/4, Technische Thermoplaste – Polyamide [Engineering thermoplastics – Polyamides], published by Carl Hanser Verlag, 1998

Test standards

Determination of mechanical characteristic values

- ISO 527-1: Plastics – Determination of tensile properties – Part 1: General principles

- ISO 527-2: Plastics – Determination of tensile properties – Part 2: Test conditions for molding and extrusion plastics

- ISO 179-1: Plastics – Determination of Charpy impact properties – Part 1: Non-instrumented impact test

- ISO 179-2: Plastics – Determination of Charpy impact properties – Part 2: Instrumented impact test

Testing for stress cracking resistance

- ISO 22088-3: Plastics – Determination of resistance to environmental stress cracking (ESC) – Part 3: Bent strip method

Corrosion testing

- VDA 230-214: Beständigkeit metallischer Werkstoffe gegen Kondensat-Korrosion in abgasführenden Bauteilen – Prüfmethode [Resistance of metallic materials to condensate corrosion in exhaust gas-carrying components – Testing methods]

Test fuels

- ISO 1817: Rubber, vulcanized or thermoplastic – Determination of the effect of liquids

- SAE J1681: Gasoline, Alcohol, and Diesel Fuel Surrogates for Materials Testing

Conditioning of polyamides

- ISO 1110: Plastics – Polyamides – Accelerated conditioning of test specimens

BASF brochures

- Ultramid® brochure, 2010
- Conditioning of finished parts made of Ultramid®, 2010
- Ultradur® brochure, 2010
- Ultraform® brochure, 2010

More information regarding the chemical behavior of Ultrason® (PSU, PESU, PPSU) can be found in the BASF brochure “Ultrason® – Resistance to Chemicals”, 2010.

Overview

Table 4: Overview of the media resistance of Ultramid®, Ultradur® and Ultraform®

	Ultramid® A	Examples	Ultramid® B	Examples	Ultramid® S
Highly resistant: empirical value from numerous applications under their typical conditions	**aliphatic hydrocarbons**	natural gas, fuels (Otto, diesel), paraffin oil, motor oils, technical greases and lubricants	**aliphatic hydrocarbons**	natural gas, fuels (Otto, diesel), paraffin oil, motor oils, technical greases and lubricants	**aliphatic hydrocarbons**
	aromatic hydrocarbons	benzene, toluene	**aromatic hydrocarbons**	benzene, toluene	**aromatic hydrocarbons**
	alkalis	ordinary soap, washing solutions, alkaline concrete	**alkalis**	ordinary soap, washing solutions, alkaline concrete	**alkalis**
	ethylene glycol	brake fluids, hydraulic fluids			**ethylene glycol**
	ethers	THF, antiknock agents for fuels (TBME, ETBE)	**ethers**	THF, antiknock agents for fuels (TBME, ETBE)	**ethers**
	esters	greases, cooking oils, motor oils, surfactants (e.g. sodium dodecyl sulfate)	**esters**	greases, cooking oils, motor oils, surfactants (e.g. organic phosphoric acid ester)	**esters**
	aliphatic alcohols	<60°C [<140°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels (E10, E50, E90)	**aliphatic alcohols**	<60°C [<140°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels (E10, E50, E90)	**aliphatic alcohols**
	water and aqueous solutions	drinking water, seawater, beverages	**water and aqueous solutions**	drinking water, seawater, beverages	**water and aqueous solutions**
	organic acids	in the solid state: citric acid, benzoic acid	**organic acids**	in the solid state: citric acid, benzoic acid	**organic acids**
	oxidants	ozone as a component of air	**oxidants**	ozone as a component of air	**oxidants**
Somewhat resistant: known applications, thorough testing and case-to-case evaluations necessary	**alkalis**	sodium hydroxide solution, ammonia solution, urea solution, amines	**alkalis**	sodium hydroxide solution, ammonia solution, urea solution, amines	**alkalis**
	ethylene glycol	coolants			**ethylene glycol**
	esters	transmission oils, biodiesel	**esters**	transmission oils, biodiesel	**esters**
	aliphatic alcohols	>60°C [>140°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels	**aliphatic alcohols**	>60°C [>140°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels	**aliphatic alcohols**
	water and aqueous solutions	chlorinated drinking water	**water and aqueous solutions**	chlorinated drinking water	**water and aqueous solutions**
	organic acids	as an aqueous solution: acetic acid, citric acid, formic acid, benzoic acid	**organic acids**	as an aqueous solution: acetic acid, citric acid, formic acid, benzoic acid	**organic acids**
	oxidants	traces of ozone, chlorine or nitrous gases	**oxidants**	traces of ozone, chlorine or nitrous gases	**oxidants**

Note: Discoloration of the test specimens is not taken into consideration during the evaluation of the resistance.

Examples	Ultramid® T	Examples	Ultradur®	Examples	Ultraform®	Examples
natural gas, fuels (Otto, diesel), paraffin oil, motor oils, technical greases and lubricants	**aliphatic hydrocarbons**	natural gas, fuels (Otto, diesel), paraffin oil, motor oils, technical greases and lubricants	**aliphatic hydrocarbons**	natural gas, fuels (Otto, diesel), paraffin oil, motor oils, technical greases and lubricants	**aliphatic hydrocarbons**	natural gas, fuels (Otto, diesel), paraffin oil, motor oils, technical greases and lubricants
benzene, toluene	**aromatic hydrocarbons**	benzene, toluene	**aromatic hydrocarbons**	benzene, toluene (severe swelling possible at elevated temperatures)	**aromatic hydrocarbons**	benzene, toluene
ordinary soap, washing solutions, alkaline concrete	**alkalis**	ordinary soap, washing solutions, alkaline concrete			**alkalis**	ordinary soap, washing solutions, alkaline concrete
brake fluids, hydraulic fluids, coolants	**ethylene glycol**	brake fluids, hydraulic fluids			**ethylene glycol**	brake fluids, hydraulic fluids
THF, antiknock agents for fuels (TBME, ETBE)	**ethers**	THF, antiknock agents for fuels (TBME, ETBE)			**ethers**	antiknock agents for fuels (TBME, ETBE)
greases, cooking oils, motor oils, surfactants (e.g. sodium dodecyl sulfate)	**esters**	greases, cooking oils, motor oils, surfactants (e.g. sodium dodecyl sulfate)	**esters**	greases, cooking oils, motor oils	**esters**	greases, cooking oils, motor oils, surfactants (e.g. sodium dodecyl sulfate), biodiesel
<60°C [<140°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels (E10, E50, E90)	**aliphatic alcohols**	<60°C [<140°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels (E10, E50, E90)	**aliphatic alcohols**	<40°C [<104°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels (E10, E50, E90)	**aliphatic alcohols**	<60°C [<140°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels (E10, E50, E90)
drinking water, seawater, beverages, road salt, calcium chloride and zinc chloride solutions	**water and aqueous solutions**	drinking water, seawater, beverages, road salt, calcium chloride and zinc chloride solutions	**water and aqueous solutions**	<40°C [<104°F] drinking water, seawater, beverages, road salt, calcium chloride and zinc chloride solutions, moist climate	**water and aqueous solutions**	drinking water, seawater, beverages
in the solid state: citric acid, benzoic acid	**organic acids**	in the solid state: citric acid, benzoic acid	**organic acids**	in the solid state: citric acid, benzoic acid	**organic acids**	in the solid state: citric acid, benzoic acid
ozone as a component of air	**oxidants**	ozone as a component of air	**oxidants**	ozone as a component of air	**oxidants**	ozone as a component of air
sodium hydroxide solution, ammonia solution, urea solution, amines	**alkalis**	sodium hydroxide solution, ammonia solution, urea solution, amines	**alkalis**	weakly alkaline media: urea solution, sodium hydroxide solution pH 10	**alkalis**	sodium hydroxide solution, ammonia solution, urea solution, amines
coolants	**ethylene glycol**	coolants			**ethylene glycol**	coolants
					ethers	tetrahydrofurane (THF)
transmission oils, biodiesel	**esters**	transmission oils, biodiesel	**esters**	transmission oils, biodiesel		
>60°C [>140°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels	**aliphatic alcohols**	>60°C [>140°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels			**aliphatic alcohols**	>60°C [>140°F] ethanol, methanol, isopropanol, anti-freeze agents for windshield washing systems, spirits, fuels
chlorinated drinking water	**water and aqueous solutions**	chlorinated drinking water	**water and aqueous solutions**	40°C to 90°C [104°F to 194°F] moist climate	**water and aqueous solutions**	chlorinated drinking water, aqueous zinc chloride solutions
as an aqueous solution: acetic acid, citric acid, formic acid, benzoic acid	**organic acids**	as an aqueous solution: acetic acid, citric acid, formic acid, benzoic acid			**organic acids**	as a diluted aqueous solution: acetic acid, citric acid, formic acid, benzoic acid
traces of ozone, chlorine or nitrous gases	**oxidants**	traces of ozone, chlorine or nitrous gases				

Overview

Table 4: Overview of the media resistance of Ultramid®, Ultradur® and Ultraform®

	Ultramid® A	Examples	Ultramid® B	Examples	Ultramid® S
Not resistant					
	mineral acids	concentrated hydrochloric acid, battery acid, sulfuric acid, nitric acid	**mineral acids**	concentrated hydrochloric acid, battery acid, sulfuric acid, nitric acid	**mineral acids**
	oxidants	halogens, oleum, hydrogen peroxide, ozone, hypo-chlorite	**oxidants**	halogens, oleum, hydrogen peroxide, ozone, hypo-chlorite	**oxidants**
Triggers stress cracking	**aqueous calcium chloride solutions**	road salt	**aqueous calcium chloride solutions**	road salt	
	aqueous zinc chloride solutions	road salt solution in contact with zinc-plated components	**aqueous zinc chloride solutions**	road salt solution in contact with zinc-plated components	
Solvents		concentrated sulfuric acid		concentrated sulfuric acid	
		formic acid 90%		formic acid 90%	
		hexafluoroisopropanol (HFIP)		hexafluoroisopropanol (HFIP)	

Note: Discoloration of the test specimens is not taken into consideration during the evaluation of the resistance.

Examples	Ultramid® T	Examples	Ultradur®	Examples	Ultraform®	Examples
			water and aqueous solutions	>90 °C [>194 °F] moist climate		
			alkalis	strongly alkaline media: sodium hydroxide solution pH 14, concrete/concrete liquor		
					sulfur dioxide	
					nitrous gases	
concentrated hydrochloric acid, battery acid, sulfuric acid, nitric acid	**mineral acids**	concentrated hydrochloric acid, battery acid, sulfuric acid, nitric acid	**mineral acids**	concentrated hydrochloric acid, battery acid, sulfuric acid, nitric acid	**mineral acids**	concentrated hydrochloric acid, battery acid, sulfuric acid, nitric acid
					organic acids	concentrated solution: acetic acid, formic acid
halogens, oleum, hydrogen peroxide, ozone, hypo-chlorite	**oxidants**	halogens, oleum, hydrogen peroxide, ozone, hypo-chlorite	**oxidants**	halogens, oleum, hydrogen peroxide, ozone, sodium hypochlorite at an elevated temperature	**oxidants**	halogens, oleum, hydrogen peroxide, ozone, sodium hypochlorite at an elevated temperature
			sodium hydroxide solution	10%-solution		
concentrated sulfuric acid		concentrated sulfuric acid				
formic acid 90%		formic acid 90%				
hexafluoroisopropanol (HFIP)		hexafluoroisopropanol (HFIP)		hexafluoroisopropanol (HFIP)		hexafluoroisopropanol (HFIP)
				dichlorobenzene/phenol (50/50)		
						N-methyl-pyrrolidone (NMP) at an elevated temperature
						dimethyl formamide (DMF) at an elevated temperature

Selected Product Literature:

- Ultramid® – Product Brochure
- Ultramid® – Product Range
- Ultradur® – Product Brochure
- Ultradur® – Product Range
- Ultraform® – Product Brochure
- Ultraform® – Product Range
- Ultramid®, Ultradur® and Ultraform® – Resistance to Chemicals

Note

Please visit our websites:
www.plasticsportal.com (World)
www.plasticsportal.eu (Europe)

Additional information on specific products:
www.plasticsportal.eu/name of product
e. g. www.plasticsportal.eu/ultramid

Request of brochures:
PM/K, F204
Fax: +49 621 60-49497

If you have technical questions on the products, please contact the Ultra-Infopoint:

Ultra Infopoint
+49 621 60-78780
ultraplaste.infopoint@basf.com

PME 1604 BE