Hydrolysis resistant PBT that withstands hot/moist environmental conditions is the preferred material for plugs, plug connectors and housings for electronic components in automobiles (photo: BASF/Bosch)

Avoiding Moisture Damage

Hydrolysis Resistant PBT. Thermoplastic polyesters such as polybutylene terephthalate are materials that are sensitive to hydrolysis. Moisture, particularly at high temperatures, damages them. Particularly in the case of electronic components in automobiles this can be critical. A specific modification of the polyester for moisture and hydrolysis resistance can help here. The effectiveness of this modification was investigated based on changes in mechanical properties and molar mass.

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The demands of the automotive industry on components are increasing continuously and thus time and again raise new challenges for the materials used. That means that plugs, plug connectors and housings for electronic components **(Title picture)** as well as overmolded sensors for under the hood applications which are often made from polybutylene terephthalate (PBT) have to pass even harder tests. Moisture – particularly at higher temperatures – damages PBTs and therefore alters their material properties. Processors of PBT know only too well that moisture and temperature can be critical since without adequate predrying of the pellet, components fresh out of the injection molding tool can be brittle and unusable. However, at temperatures under 100 °C the damaging effect of moisture only makes itself noticeable later on. Under typical terrestrial climatic conditions even PBTs without any special modification can retain practically constant properties over many years. However, in automobiles at least sometimes temperature and moisture conditions that are much more demanding than natural weathering can be found. For this reason many specifications require testing at 85 °C and 85 % relative humidity.

For applications with high demands on moisture resistance BASF SE, Ludwigshafen, Germany, has developed special grades of PBT which allow components with many times the service life of those made from conventional grades to be produced. These materials are available with 30 % glass fiber reinforcement under the brand name of Ultradur B4330 G6 HR and with 15 % glass fiber reinforcement as Ultradur B4330 G3 HR. The suffix HR stands for hydrolysis resistant. Hydrolysis is the chemical term for the reaction between water and polyester that damages the material.

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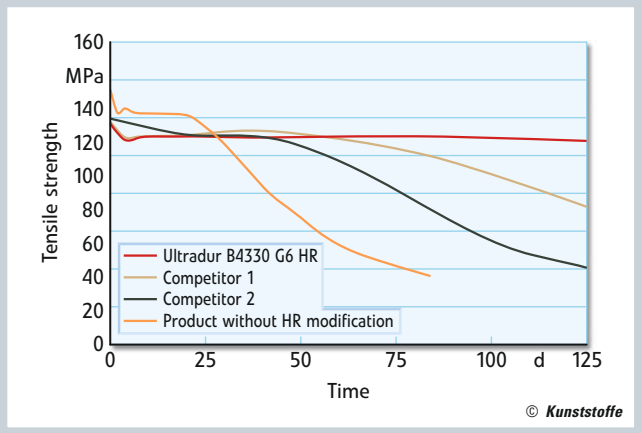
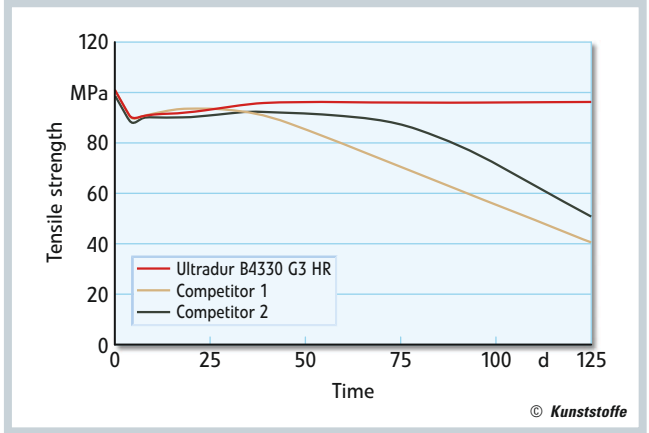
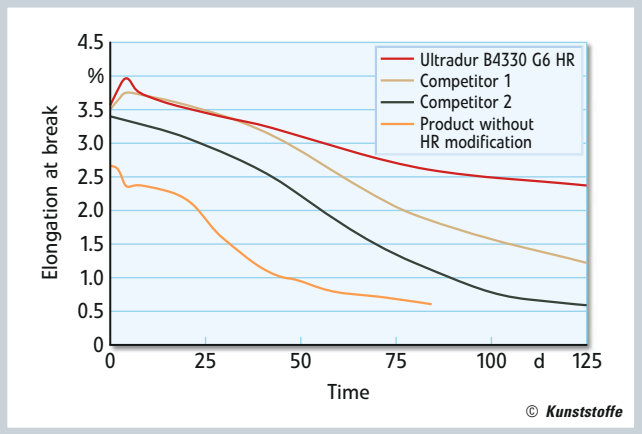
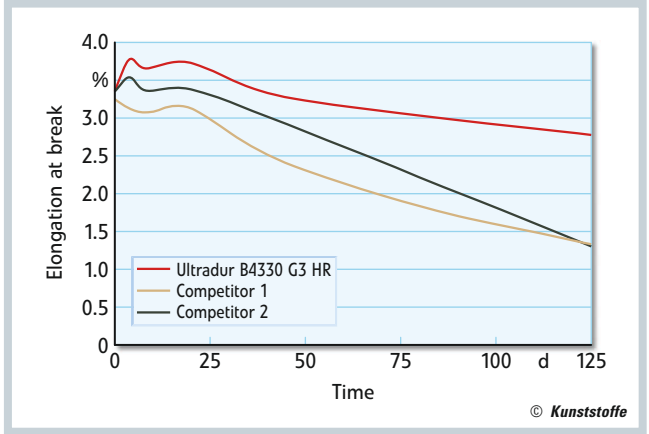
Tests and Materials

In order to test the hydrolysis resistance of various PBTs test bars were injection









Figs. 1 to 4. Comparison of tensile strength and elongation at break of various PBT GF15 and 30 grades (with and without hydrolysis stabilization) that were stored at 85 °C and 85 % relative humidity (r.h.) for 125 days (figs. 1 to 8: BASF)

molded and held in a climate chamber at a temperature of 85 °C and a relative humidity of 85 %. The standard length of storage for the test pieces was 3,000 h (125 days); samples were taken and characterized every 500 to 1,000 h. The investigations followed the tensile properties, impact strength and viscosity numbers. The latter is a measure of the average chain length and allows hydrolysis to be observed at a chemical level. Three materials with 15 and 30 % glass fiber reinforcement, marketed by their manufacturers as hydrolysis resistant, were tested. These included the two Ultradur HR grades mentioned above as well as two competitive products with the appropriate levels of reinforcement. For comparison products without HR modification were also included in the investigations.

Changes in Properties

The stiffness of the materials investigated did not change significantly during the 3,000 h under the influence of the hot and humid environment. The reason for this is that during the tensile tests used to determine the E-modulus the materials are only stretched by a very small amount. The forces and stresses applied to the material can be adequately distributed even by very short chained molecules.

However, things look very different when considering tensile strength and elongation at break **(Figs. 1 to 4)**. To determine these values the tensile test bars are stretched to their failure point, which is after all by several percentage points. Optimal strength in this case can only be achieved if sufficiently long polymer chains are present. If due to hydrolysis the chains are too short then their ability to uniformly distribute stress is reduced and the material fails at lower tensile strength values.

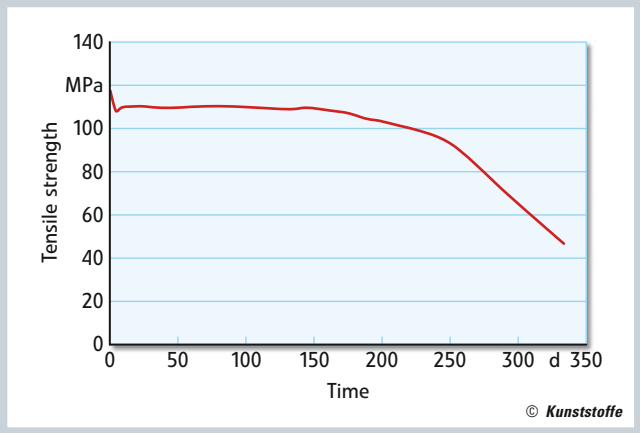
Since the properties of the hydrolysis stabilized Ultradur grades had barely changed over the whole of the 125 days (3,000 h) in the elevated temperature and humidity of the climate chamber, the testing time of the Ultradur B4330 G6 HR was increased to 8,000 h in order to establish the limits of the material **(Figs. 5 to 6)**. A reduction in tensile strength occurred only after 200 to 250 days, that is after 4,800 to 6,000 h. This shows that the material is clearly more stable under these conditions than all the other grades and can in this respect meet extremely strict testing requirements.

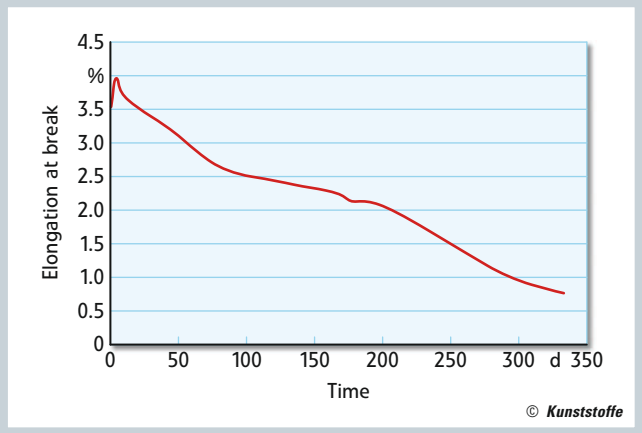
The Influence of Wall Thickness

There are two limiting cases for polymer hydrolysis. Where the water quickly and uniformly saturates the polymer hydrolysis occurs in all locations at the same time and at the same speed. If the water cannot penetrate the polymer, hydrolysis occurs only at the surface where material is removed layer by layer. In real world systems however, both processes are found running alongside one another. Which process dominates when is already known from the literature [1]. In the case of PBT it can be shown that aging at 85 °C and 85 % relative humidity overwhelmingly follows the former mechanism (uniformly throughout the entire volume of the test piece): Tensile test bars with a thickness of 0.8, 1.6, 3.2 and 4.0 mm all aged at practically the same rate. This means that the results obtained for the standard test bars with a thickness of 4 mm should be transferable to thinner walled components as well.

Focusing on the Polymer Chains

Since hydrolysis breaks bonds in the main polymer chain the resulting fragments are shorter, i. e. they have a lower (average) →





Figs. 5 to 6. Determination of tensile strength and elongation at break of the hydrolysis resistant Ultradur B4330 G6 HR grade of PBT that was stored at 85 °C and 85 % r.h. for 350 days

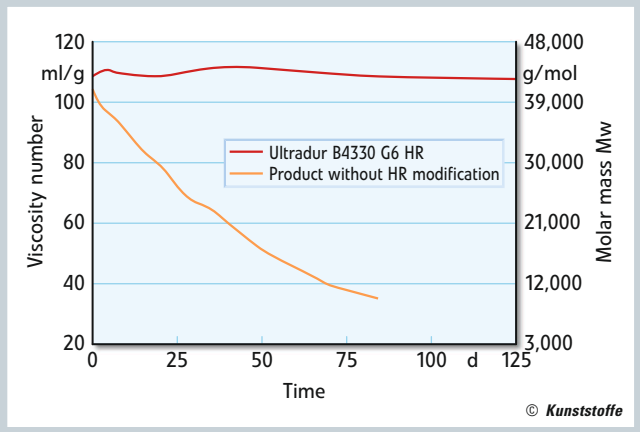


Fig. 7. Investigation of the viscosity number / molar mass of the hydrolysis resistant Ultradur B4330 G6 HR in comparison to non hydrolysis stabilized 30 % GF reinforced PBT at 85 °C and 85 % r.h.

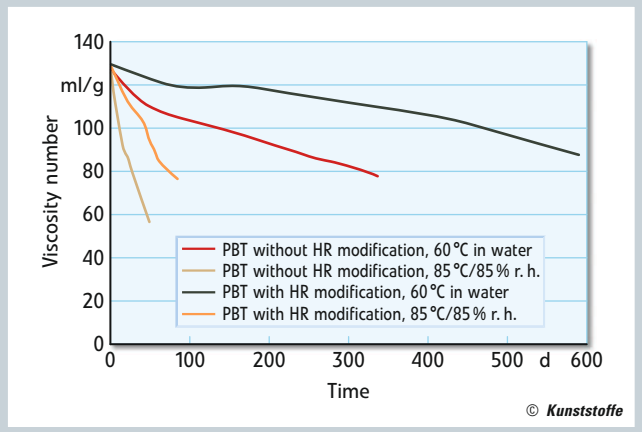


Fig. 8. Investigation of the viscosity number of unreinforced PBT products with and without hydrolysis stabilization under different storage conditions

molar mass. One measure of the average molar mass is the viscosity number [2] which is easy to measure. In the relevant regions molar mass and viscosity numbers have a nearly linear relationship to one another and so in **Figure 7** both values are given on the Y axes. The products shown – Ultradur B4330 G6 HR and a reference material without HR modification – have very different behavior. For PBT without HR modification a reduction in the molar mass occurs almost immediately whilst the HR grade stays at a constant level. The mechanical properties **(see Figs. 1 and 3)** do not however react instantaneously to the changes in viscosity number.

Temperature and Moisture

Fundamental research into the influence of temperature and humidity on the hydrolytic aging of PBT materials were published more than 30 years ago [3]. The empirical determination of hydrolytic aging faces two difficulties. Firstly aging data are needed for storage at low temperature and relative humidity, where aging takes many years to occur, and secondly these time consuming aging tests have in principle to be carried out individually for each product since fillers and additives influence the rate of hydrolysis through complex interactions.

In **Figure 8** the effect of hydrolysis retarding additives under different conditions is shown on the basis of unreinforced PBT model compounds. In all cases the viscosity number continuously declines from the very beginning. However, at 85 °C and 85 % relative humidity the reduction occurs many times faster than in water at 60 °C. If the environment continuously provides plenty of water the rate of hydrolysis is highly dependent on the temperature. In both cases however, the HR modification helps to significantly slow the aging process. The results of time lapse testing at 85 °C and 85 % relative humidity are thus indeed semi-quantitatively transferable to less demanding conditions.

Conclusion

Ultradur HR grades from BASF are optimized PBT materials that are able to withstand hydrolysis in moist environmental conditions. These grades are significantly more resistant than products without HR modification and also have an advantage in comparison to competitive HR modified materials. Ultradur HR can therefore be used to make components with particularly long service lives that can also survive use under aggressive conditions. ■

REFERENCES

1 Bellenger et al., Polymer Degradation and Stability, 1995, Vol. 49, pp. 91
2 Horbach et al., Die Angewandte Makromolekulare Chemie, 1981, Vol. 98, pp. 35
3 Gardener et al., Journal of Applied Polymer Science, 1980, Vol. 25, pp. 2353

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