The housing of the electronic control for clutch transmissions is often made of PBT (photo: BASF)

Testing Gets Tougher

Hydrolytically Stable PBT. The requirements on automotive plastic parts, especially, keep growing tougher. The stability of the parts is particularly threatened by extreme temperatures and a damp environment. Two newly developed hydrolytically stable PBT compounds have come through a number of tests, some of which were very tough.

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The requirements imposed by the automotive industry on parts continue to rise and so are also creating fresh challenges for the constituent materials. Plugs, connectors and housing parts that are used under the hood are having to pass even tougher tests. Cycle tests in humid conditions and temperatures ranging from -40 to 150 °C are no rarity and require materials treated with special hydrolysis stabilizers. To meet these high standards, BASF developed and evaluated two hydrolysis-resistant PBT compounds in different and, in some cases, very tough tests. The two new products are Ultradur B4300G6 HR and Ultradur B4330G6 HR and each is reinforced with 30 % glass fiber. HR stands for hydrolysis resistant.

Water Destroys the Polymer

PBT is formed by polycondensation of terephthalic acid or dimethyl terephthalate and 1,4-butanediol, with the release of water. However, the polycondensation reaction can be reversed by hydrolysis at temperatures exceeding 100 °C and 100 % relative humidity (Fig. 1). In the reaction between PBT and water, the polymer chain is cleaved and fragments, ranging from small chains right through to the starting materials terephthalic acid and 1,4-butanediol, are formed. This means that the esterification can be reversed (deesterification). It only takes a hydrolyzed content of 0.01 % to significantly degrade the viscosity and the molar mass. Hydrolytic destruction of the polymer by catalysts is 1,000 and 10,000 times as fast as thermal oxidation and thermal decomposition. Hydrolysis may be halted or at least retarded by adding various stabilizers. Conventional stabilizers are capable of scavenging the water on one hand and rebuilding destroyed polymer chains on the other.

The chosen study conditions described in more detail below simulate extreme situations and far exceed those actually found under the hood of a vehicle. Since the underhood area is generally well ventilated, the headwind can dissipate both local moisture and evolved heat and so a protracted period of high atmospheric humidity combined with high temperature is rather unlikely there. This may be seen in Figure 2: it shows the viscosity of a standard PBT containing 30 % glass fibers which does not undergo any hydrolytic degradation on storage either at 50 °C and 75 % relative humidity or at 60 °C in water. Only when the temperature reaches 85 °C and the relative humidity is 85 % does hydrolysis occur.

Passing the USCar Test

The USCar test is a set of regulations for the American automotive industry. Among other things, the USCar test contains a test method for qualifying electrical connectors and connector systems which has been agreed by the three major American car manufacturers Ford, Chrysler and GM and which therefore may be regarded as an industry standard.

In this test method, standardized test rods are conditioned by exposure to a stringent temperature and relative humidity cycle and the mechanical proper-

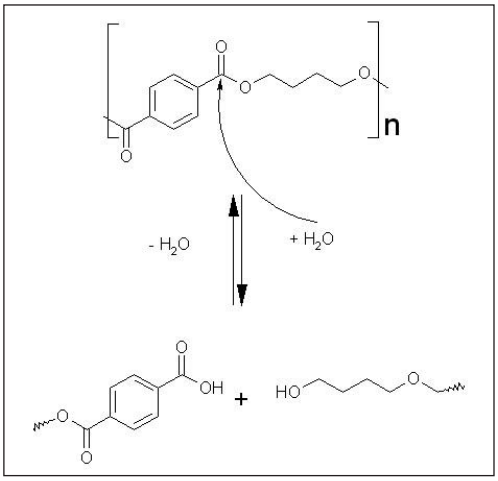

Fig. 1. Mechanism underlying the hydrolysis of polybutylene terephthalate (PBT)

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ties before and after conditioning are compared. In accordance with the outcome, the product is assigned to one of Connector Classes I to IV. Each sample of material for testing is first exposed for 30 minutes to a temperature of -40 °C and a relative humidity of 0 to 10 %. Within 60 minutes, the temperature must rise to 80–90 °C; the relative humidity must be 95 % (up from 85 %). These parameters are maintained until hour 5. Subsequent testing then depends on the classification. Whereas the relative humidity for all samples must be reduced to 0–10 % by hour 7 at the latest, the maximum temperature for test hours 5 to 7 varies according to Connector Class: 85 °C for Class I, 100 °C for class II, 125 °C for Class III and 155 °C for Class IV. From hour 8, the temperature in all cases must be -40 °C again, because a new test cycle then commences. Such 8-hour cycles are repeated 40 times to produce a total conditioning time of 320 hours (Fig. 3). If the mechanical properties of the conditioned specimens are still more than 80 % of their initial values, the material is assigned to the Connector Class corresponding to that conditioning temperature. The two new products Ultradur B4300G6 HR and Ultradur B4330G6 HR passed the requirements of USCar PF-1 Class III in tests performed by external US institutes.

Since the regulations on hydrolysis resistance in the electrical area are not standardized, several manufacturers specify tests for resistance to certain air humidity-temperature conditions, aside from the USCar test. These include resistance in alkaline solution under flexural stress and a number of very tough relative humidity/conditioning tests. Two standard products from the BASF range, natural (nat) and black (b), as well as Ultradur B4330G6 HR (nat) and Ultradur B4330G6 HR (b), i.e. the new Ultradur HR hydrolysis-resistant products, were subjected to four different test regimes. The tests were performed on tensile rods compliant with ISO 527 and Charpy rods compliant with ISO 179 that were injection molded from each material. The blank value of the physical properties was determined a few days after production because the test specimens first had to be dry conditioned.

Loading with 2 and 2.78 % Flexural Stress

In the wetting test at 2 % flexure, the injection molded tensile rods are clamped to a metal cylinder which flexes them by 2 %. The cylinder has a radius of 50 mm and is made according to DIN EN ISO 4599. Conditioning in 10 % sodium hydroxide (NaOH) solution consists in wetting the specimens with this solution for the first 60 minutes at 10-minute intervals. Three specimens of each material are clamped for this. After conditioning for 2 and 24 hours, they are examined for stress cracking (Fig. 4).

A similar test set-up flexes the test specimens at 2.78 %. Unlike the 2 % flexure test, the specimens in this method are immersed along with the holding device in a bath containing 10 % sodium hydroxide solution.

Conditioning under Different Conditions

85 °C and 85 % relative humidity: The test specimens are kept in a climate cupboard in hydrolytic conditions of 85 °C and 75 % relative humidity. After conditioning for 4, 8 and 41 days, their mechanical properties are tested. To obtain the most accurate mean value of these properties as possible,10 test specimens of each product are stored for every time period; in other words, 10 × 4 × 3 = 120 tensile rods complying with ISO 527-2 and 120 Charpy rods complying with ISO 179.

110 °C and 100 % relative humidity: here, the test specimens are stored in a type of steam pressure cooker and the specified conditions are created by adding roughly one liter of distilled water and the use of a hot plate. Tests are scheduled after four and eight days. Here, too, 10 test specimens of each product are used for each sampling (after four days and after eight days).

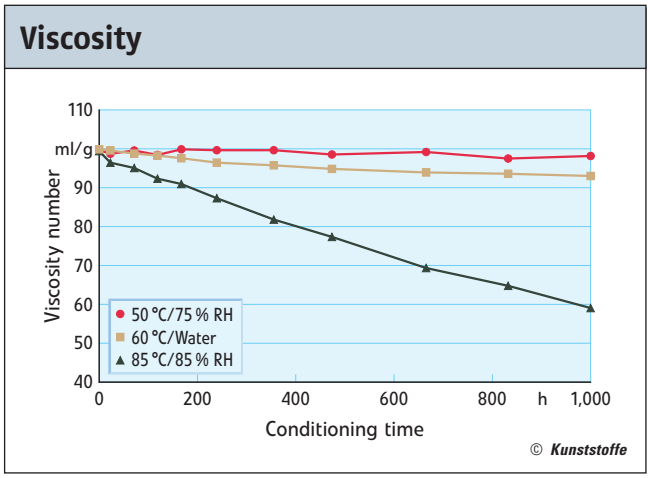

Fig. 2. Decrease in viscosity due to hydrolysis of PBT under various conditions (RH: relative humidity)

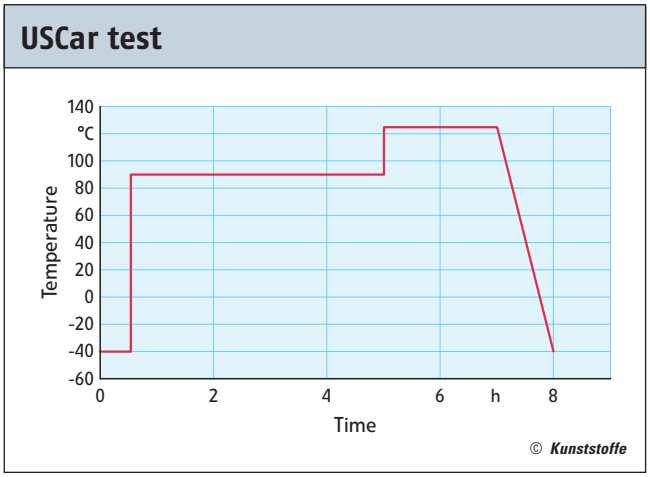

Fig. 3. Temperature change for USCar PF-1 Class III

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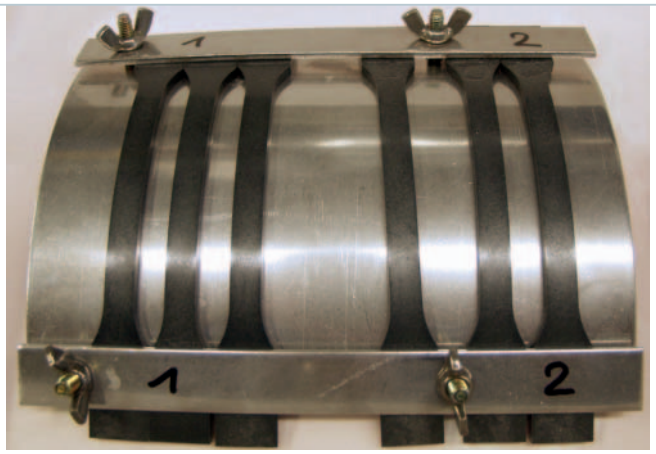

Fig. 4. Test rig according to DIN EN ISO 4599

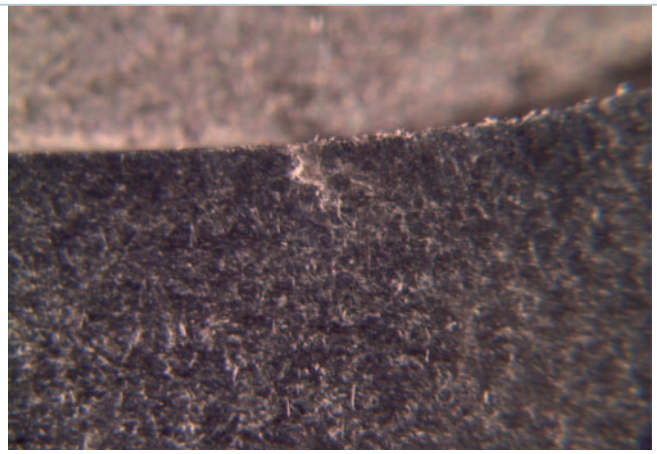

Fig. 5. Electron micrograph of specimen of Ultradur B4330G6 HR (b) after 24 hours conditioning in the 2 % flexural stress test

Results

For the 2 % flexure test, three tensile specimens of each material were subjected to the flexural stress test of ISO 4599. Some of the standard rods broke within 2 hours and all broke within 24 hours. The new, hydrolytically stabilized PBT grades Ultradur B4330G6 HR (nat) und B4330G6 HR (b) exhibit comparatively high resistance to sodium hydroxide at room temperature. Compared with the standard, these products develop stress cracking only after 24 hours (Fig. 5).

The test results for 2.78 % flexure confirm the very good hydrolysis resistance of the Ultradur HR products in comparison with the competition products as well. Whereas the two competition products break within 10 seconds at most after contact with the sodium hydroxide solution, Ultradur B4330G6 HR still shows no sign of fracture even after 52 hours.

Following conditioning under the conditions described, B4330G6 HR (b) exhibits very good hydrolysis-resistance across all mechanical properties, never sustaining a loss of more than 20 % of its initial values. The standard product becomes useless after eight days' hydrolysis conditioning under these more exacting conditions, as the mechanical values drop by roughly 70 %. The mechanical properties of B4300G6 HR (b), too, deteriorate much less in this extremely exacting test. The new B4300G6 HR variant survives both studies, namely the Charpy impact test following conditioning at 85 °C and 85 % relative humidity (Fig. 6) and the elongation at break test at 110 °C/110 % relative humidity (Fig. 7), virtually undamaged.

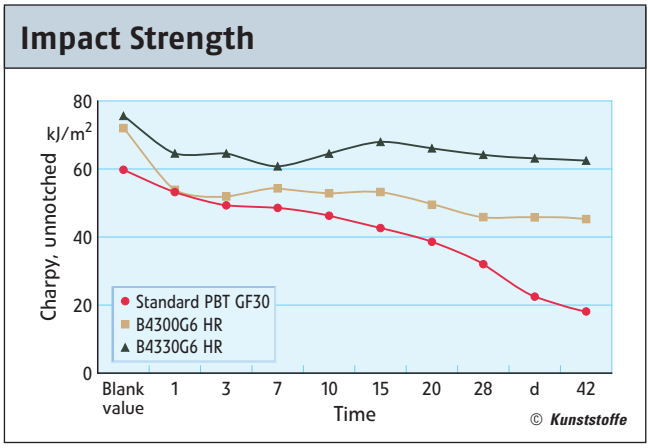

Fig. 6. Charpy impact strength (unnotched) after conditioning at 85°C / 85% relative humidity

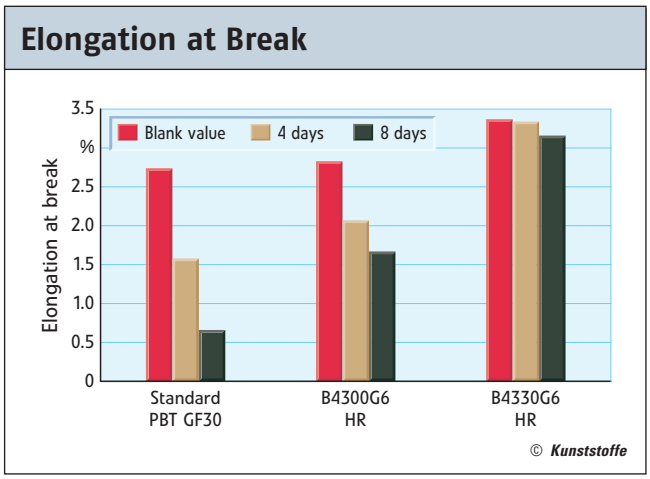

Fig. 7. Elongation at break after conditioning at 110 °C / 100 % relative humidity

Conclusion

The new materials display extraordinarily good results under extremely exacting hydrolysis conditions for standard tensile rods and Charpy rods. The new Ultradur B4330G6 HR is particularly recommended for the kind of pre-stress that occurs in sheathed metal jacks; it also exhibits a higher resistance to 10 % sodium hydroxide at room temperature. The new Ultradur HR product series greatly extends the range of applications for PBT under extreme conditions and enables processors to comply with the ever higher specifications and new standards imposed by automotive manufacturers on their parts. ■

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