All commercial vehicles over 6 t total weight from DaimlerChrysler are fitted with the Bluetec exhaust gas cleaning system based on SCR
(photo: DaimlerChrysler)

Materials for Clean Diesel Engines

Engineering Plastics. Selective catalytic reduction technology (SCR) can significantly help to cut nitrogen oxide emissions from diesel engines through the use of an aqueous urea solution. This opens up another field of application for engineering plastics, in which they will have to meet new chemical resistance requirements.

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Whether it is California's LEV II emission standards or the impending Euro 5 exhaust gas regulations, the legislative conditions under which motor vehicles with internal combustion engines have to operate are tightening, so providing automotive manufacturers and suppliers with further impetus for innovation. In simple terms, the task of engineers in this situation is to reduce the fuel consumption of gasoline engines to the significantly lower level of diesel units and to make self-igniting diesel engines as clean as their gasoline counterparts.

Emission Limits and Standards

Diesel engines, in particular, are the subject of numerous development activities, because their specific emissions of carbon black particles (fine dust) and nitrogen oxides (NO_x) are currently giving rise to public debate and legislators are set-

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Fig. 1. Tank module made from POM: the material combines very high fuel and chemical resistance with good long-term heat resistance and electrical insulation properties

ting high requirements. For example, the maximum permissible emission limits for diesel vehicles up to 3.5 t under the current Euro 4 exhaust gas standard are 0.025 g/km for fine dust and 0.25 g/km for nitrogen oxides. The Euro 5 standard, which comes into force in September 2009, will set even lower limits for this vehicle class. For NO_x emissions, a reduction by more than 20 % to 0.18 g/km has been decided. Particle emissions will come down to only 0.005 g/km, as is also proposed in the US LEV II draft. This represents a reduction of over 80 % as compared with the Euro 4 standard. In the case of heavy goods vehicles, for which emissions are quoted in the unit g/kWh, the Euro 4 standard specifies a nitrogen oxide emission limit of 3.5 g/kWh. Under the Euro 5 standard, a limit value of only 2.0 g/kWh is to be introduced.

It will not be possible to meet these ambitious targets with today's technologies. A combination of very different innovations from the areas of heat management, combustion technology, turbocharging, exhaust gas recirculation and exhaust gas aftertreatment will be required.

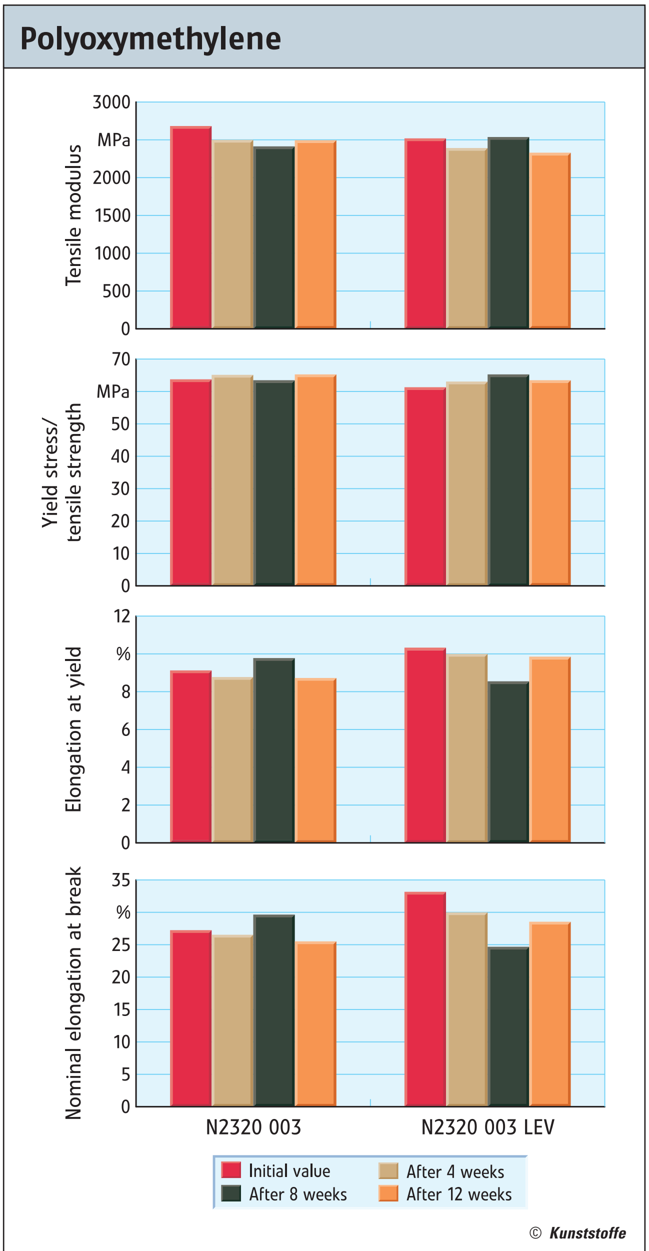

Fig. 2. Change in the mechanical properties of Ultraform N2320 003 and Ultraform N2320 003 LEV after immersion in AdBlue at +60 °C

Reducing Nitrogen Oxides in Exhaust Gas

While particulate filters reduce the fine dust emissions of a diesel engine, automotive manufacturers are relying on the new SCR process (Selective Catalytic Reduction) with AdBlue to combat nitrogen oxides. AdBlue is an ultrapure, aqueous urea solution, which is carried in an additional reservoir and acts as a reducing agent. AdBlue is injected under high pressure via a metering valve into the pre-cleaned exhaust gas stream. The heat of the exhaust gas causes it to decompose into ammonia, which then passes into a downstream catalytic converter, where it reduces the nitrogen oxides into harmless nitrogen and water. As one of the leading urea producers, BASF AG includes AdBlue in its product range.

DaimlerChrysler became the first vehicle manufacturer to offer exhaust gas cleaning based on SCR, when it introduced its Bluetec system at the beginning of 2005 for all commercial vehicles over 6 t total weight (Title picture). According to information from the company, over 20,000 vehicles are already fitted with the technology and meet the Euro 5 standard. Scania, MAN, DAF, Iveco, Renault and Volvo trucks are also using SCR technology based on AdBlue. And the use of urea technology for cars is now also on the horizon. According to an announcement by the Mercedes car group, the E 320 model will be the first series-production car to be fitted with Bluetec. Initially available only in North America, the Bluetec car will also be on the market in Europe by 2008. So far, vehicles have mostly been filling up with AdBlue at the depots of haulage and bus companies. For future requirements, a wide network of filling stations will have to be established.

Materials and Applications

The classic advantages of plastic as a material can also be exploited in SCR systems based on AdBlue: mouldability into virtually any shape, light weight and very low specific costs for long runs. Many established metals and also the usual types of glass cannot be used because of their insufficient resistance to AdBlue and/or a high risk of contamination of AdBlue in direct contact with the urea solution. These metals include copper, copper-containing alloys, zinc, iron, unalloyed and galvanised steels as well as aluminium and its alloys.

Many of the numerous devices and containers on board of a vehicle that may come into contact with AdBlue can be produced from plastic:

- storage reservoirs/tanks and their closures,
- ventilation devices,
- filling level measuring devices,
- feed devices, pumps for AdBlue or compressed air,
- pipelines, hoses,
- electrical and hose connectors, hose couplings,
- filters,
- valves,
- metering devices and
- fastening elements.

There are also similar applications in the supply infrastructure, i. e. in filling stations and gasoline pumps.

While polyolefins are particularly suitable for reservoirs and tanks, engineering plastics like polyoxymethylene copolymer (POM; Fig. 1), polyamides (especially PA 66), and polyesters like

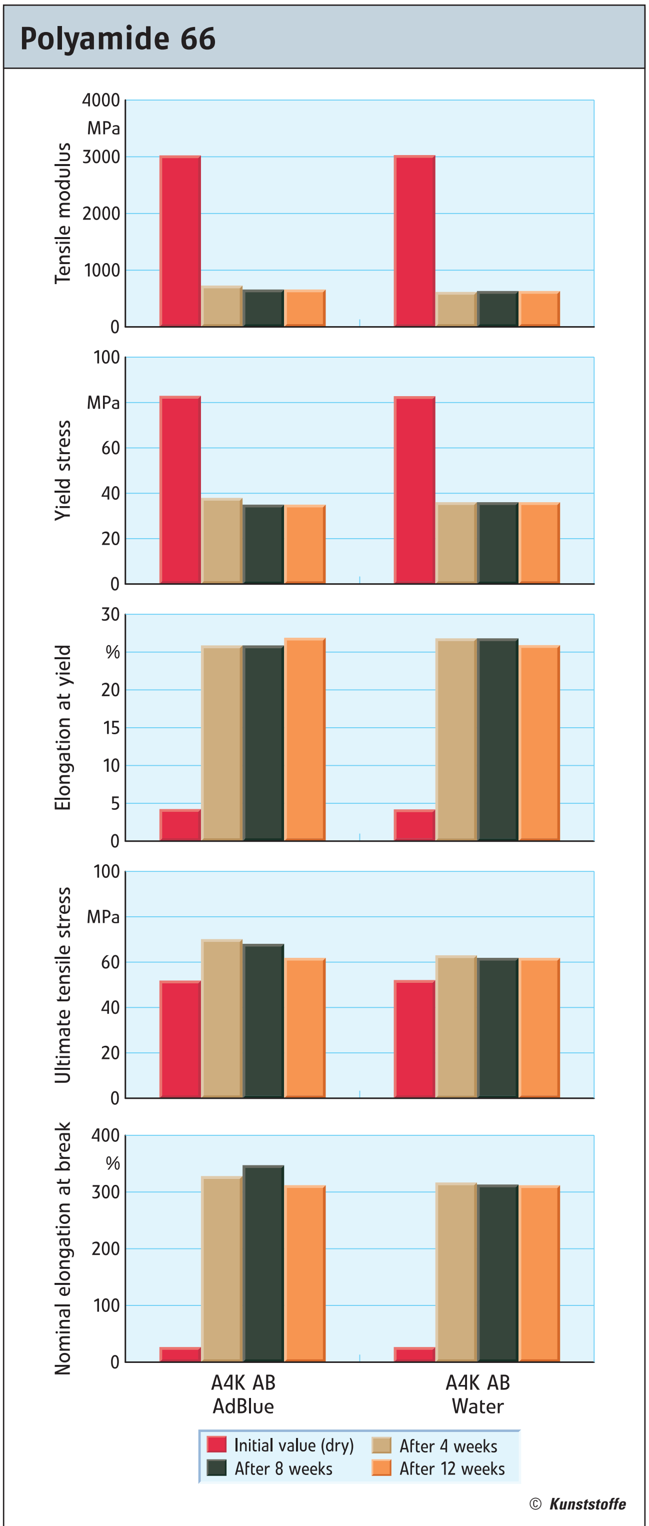

Fig. 3. Change in the mechanical properties of Ultramid A4K AB after immersion in AdBlue and water at +60 °C

polybutylene terephthalate (PBT) are preferred for most of the more challenging applications, provided that their chemical resistance meets requirements.

Plastics in Contact with Urea

What is the long-term resistance of plastics in contact with AdBlue? Urea is a polar organic compound, whose aqueous solutions have a slightly alkaline reaction. Freshly prepared solutions have a pH ranging from 9.0 to 9.5, which increases to pH 10 after storage. The possible effects of this property on the behaviour of plastic materials must be studied and taken into account. Such studies will include interactions of urea with both the polymer matrix and additives, fillers or reinforcing materials that may possibly be present. On the other hand, it is also important to ensure that the performance of the SCR system is not impaired by the use of plastics. No critical constituents may be washed out of the materials into AdBlue. The same applies to degradation products that can be formed from the plastic or its constituents after long-term contact with AdBlue. The requirements are high: AdBlue may contain a maximum of 0.5 ppm iron, calcium, magnesium, sodium and potassium, and the permissible limits for the particularly feared catalyst poisons copper, zinc, chromium and nickel are even lower at 0.2 ppm (for the sake of illustration, 0.1 ppm corresponds to 0.1 g per 1000 kg).

Studying Long-Term Behaviour

Since AdBlue is still a very young technology, no reliable body of practical experience relating to the long-term behaviour of materials in contact with urea solution is available as yet. Long-term experience in this case means the lifetime of a vehicle, i. e. about ten years (or 1 million km) for a truck and 15 years (or around 300,000 km) for a car.

There is therefore a need for a suitable accelerated test model that can yield useful information quickly on the long-term behaviour of plastics in contact with AdBlue. Possible methods for accelerating the ageing process include raising the urea content of AdBlue, increasing the material surface area in contact with AdBlue or immersion at elevated temperature. Standard accelerated test methods on the market at present work with a combination of the two latter methods. Because of its high practical relevance, the process described as follows has proved particularly successful.

4 mm-thick tensile test bars of the 1A type as per ISO 527, made from uncoloured polypropylene or polyethylene, are immersed in AdBlue at +60 °C in sealed wide-necked flasks. It is usual, for example, to immerse five tensile test bars in 1 kg of AdBlue for a period of four weeks. It is essential to ensure that within a test series only flasks produced from the same manufacturing batch are used. Before the test, the flasks are washed once with distilled water and twice with AdBlue. Parallel storage of AdBlue without the addition of test specimens is also important so as to determine the blank value, i. e. the change in the urea solution itself, and take this into account in the assessment. Tests at temperatures higher than +60 °C give rise to questionable results, because then untypically rapid decomposition of urea into ammonia and carbon dioxide takes place. In addition, from temperatures of +70 °C upwards, biuret – the dimer of urea – is also formed. On conclusion of these tests, the composition of AdBlue

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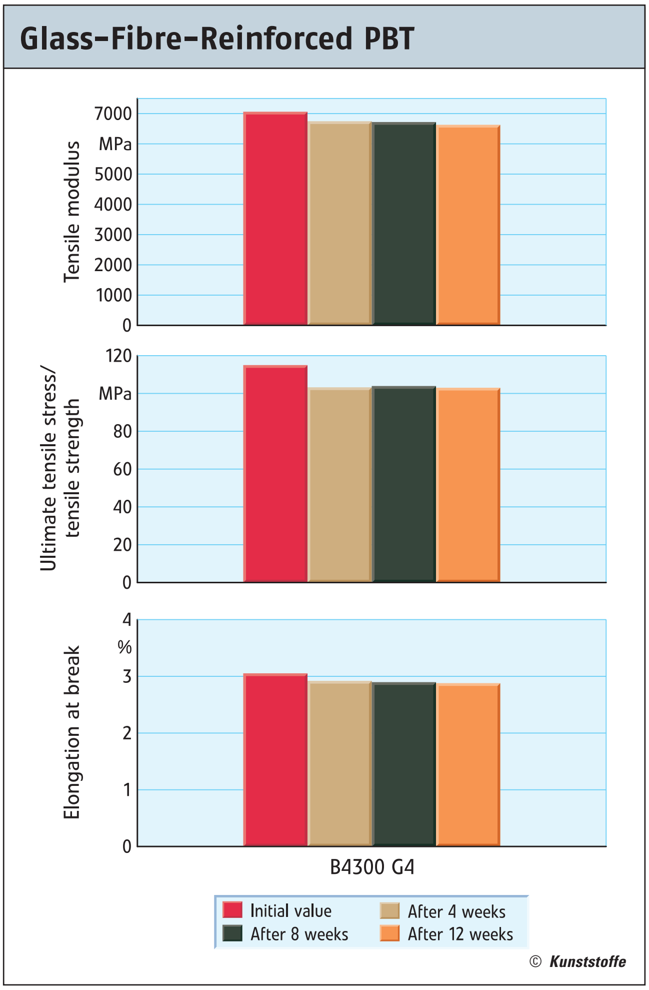

Fig. 4. Change in the mechanical properties of Ultradur B4300 G4 after immersion in AdBlue at +60 °C

is analysed according to DIN 70070 and DIN V 70071. The test specimens of the various materials undergo suitable mechanical property tests, for example the tensile test as per ISO 527.

Experience so far shows that the result of this test reproduces the effect that contact between plastic and AdBlue solution causes within a year. This is roughly based on filling the AdBlue tank in a diesel car. To simulate longer contact times, the test periods would have to be extended or other accelerated tests developed.

Results: Virtually No Changes

In the current draft of ISO 22241-3, some classes of polymer materials are already recommended as suitable for contact with AdBlue. According to this standard, these plastics do not give rise to any appreciable contamination of AdBlue, provided that they are additive-free. The recommended plastics include polyethylene, polypropylene, polyisobutylene, perfluoroalkoxy (PFA), polyfluoroethylene, polyvinylidene fluoride, polytetrafluoroethylene and copolymers of vinylidene fluoride and hexafluoropropylene. This list is not yet complete and even changes in the mechanical properties of the recommended materials cannot be categorically ruled out, so that individual commercial products must be separately tested.

The suitability of some engineering plastics not yet included in the current draft of ISO 22241-3 is therefore described below. The plastics chosen were commercial products of BASF from the following material classes:

- unreinforced POM: Ultraform N2320 003 and Ultraform N2320 003 LEV, an emission-optimised material (LEV = Low Emission Version),
- unreinforced PA: Ultramid A4K AB, a PA 66 optimised for AdBlue applications and
- glass-fibre-reinforced PBT: Ultradur B4300 G4 with a 20 % glass fibre content.

Tensile test bars of type 1A as per ISO 527, produced from the above-mentioned materials, were immersed in AdBlue solution for a total of three four-week test periods at +60 °C. Because of the significant effect of water on the mechanical properties of polyamides, the Ultramid grades were also immersed in hot water (+60 °C) in parallel tests.

As Figures 2 to 4 show, the mechanical property values of Ultraform and Ultradur over the discussed time period hardly change at all. In the case of Ultramid A4K AB, changes take place to about the same extent as would be expected after immersion in pure water. At room temperature, PA 66 absorbs up to 9 % water, while POM and PBT take up less than 1 %. In the case of PA 66, water absorption leads typically to a significant decrease in rigidity and strength accompanied by a sharp rise in elongation at break.

Analyses of the AdBlue solutions used also show that the specifications for copper, zinc, chromium, nickel, calcium, iron, aluminium, magnesium, sodium, potassium and phosphate are reliably met by all the materials tested after three storage periods.

Conclusion

The results of the long-term immersion of POM, PA and PBT engineering plastics in AdBlue solutions encourage the view that these materials could be used in AdBlue applications. This applies particularly to the thermoplastics from the BASF range studied here. Further tests on specific components must be carried out to show how far the results of accelerated test models can actually be applied to everyday practice. ■

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