Urea-resistant EPDM gaskets and hoses

VW TL 52686 – Replacement of carbon black N990 with Aktisil VM 56

M. Aufmuth, H. Oggermüller, T. Brandmeier

EPDM is used for a very wide range of applications in the automotive industry. Selective catalytic reduction has become established in making diesel engines more environmentally friendly. As an aqueous urea solution (AdBlue) is employed here, the hoses and seals in the vehicle that come into contact with this substance must have sufficient resistance to urea. Carbon black N990 is often used as a filler in such applications. This study investigates the substitution of this carbon black with Aktisil VM 56. Aktisil VM 56 is a Neuburg Siliceous Earth-based mineral filler marketed by Hoffmann Mineral GmbH. The unique structure of the siliceous earth enables results to be obtained that are not possible with carbon black N990 or other fillers alone. The substitution of carbon black N990 with Aktisil VM 56 allows, for example, a higher vulcanisation speed to be achieved, resulting in a shorter conversion time. Use of Aktisil VM 56 also enables the modulus to be significantly improved. The substitution of carbon black N990 with Aktisil VM 56 enables blooming-free products and improved collapse resistance during extrusion. The use of Aktisil VM 56 also leads to a significant reduction in the costs with identical resistance to urea.

1 Introduction

Selective catalytic reduction (SCR) for exhaust gas after-treatment using aqueous urea solution (AdBlue; AUS 32) has long established itself as a method for making diesel engines more environmentally friendly. As soon as AdBlue is injected into the hot exhaust gas stream, a hydrolysis reaction produces ammonia and CO_2. The ammonia is then required in the downstream SCR converter to transform nitrous oxides (NO_x) into water and elementary nitrogen. Once the engine and exhaust system are at operating temperature, the SCR converter removes up to 90 % of the nitrous oxide emissions from the exhaust gas. Currently (as of 2020), an estimated 20 million vehicles from German group brands are fitted with this type of exhaust gas after-treatment. Furthermore, this technology will be indispensable in meeting future limits for environmental protection [1]. The strain placed on the elastomer components by this interaction of basicity and temperature is not to be neglected, however, and a high performance of the formulation and the raw materials is crucial.

In this study, we compare Aktisil VM 56 with a thermal carbon black N990 and present the advantages of a surface-treated Neuburg Siliceous Earth. Aktisil VM 56 is based on Neuburg Siliceous Earth, a naturally occurring mixture of corpuscular, amorphous silica and lamellar kaolinite, surface-treated with a vinyl silane. Due to its property profile, Aktisil VM 56 is very popular with both clients and prospective customers. One field of application for Aktisil VM 56 is, for example, hoses and mouldings of EPDM. Here Aktisil VM 56 not only improves the vulcanisation speed or the mechanical properties of the parts, but can also prevent the efflorescence of fission products. In addition, Aktisil VM 56 can be used as a substitute for carbon black, enabling the costs to be optimised. **Figure 1** shows a REM image of the Neuburg Siliceous Earth in which the unique structure of this mineral mixture can be clearly seen. This structure and the resulting properties enable the characteristics of products with Neuburg Siliceous Earth to be improved in a way not possible with other fillers. This article presents Aktisil VM 56 as a substitute or combination partner for thermal carbon black N990. The properties changed by the substitution of carbon black are shown below.

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All figures and tables, unless otherwise stated, have been kindly provided by the authors.

2 Status quo and objective

Technical Guideline "VW TL 52686" deals with elastomer materials that are resistant to aqueous urea solution for exhaust gas after-treatment by selective catalytic reduction (SCR). It provides for the use of either an EPDM or HNBR rubber grade for seals (e.g. O-rings, TL 52686-A) and pressure/moulded hoses (TL 52686-B). The use of hydrogenated acrylonitrile butadiene rubber (HNBR) enables excellent resistance to diesel fuel to be achieved. This is necessary in case the driver of the car refuels incorrectly and as a result the components of the exhaust gas after-treatment system are flooded with fuel. Since an HNBR rubber is many times more expensive than EPDM rubber, however, and offers no other application-related advantages, these studies were carried out using an amorphous

EPDM grade. The goal of this study is to investigate and present the processing and extrusion properties, the mechanical properties, the resistance to a urea solution and last but not least the change in costs of an EPDM blend after substitution of carbon black N990 with Aktisil VM 56.

3 Experimental

3.1 Formulation, fillers, vulcanisation

When creating the formulation, attention must be paid to using as little plasticiser and additives as possible in order to avoid a potential impairment of the catalytic reduction caused by impurities released from the component. Furthermore, peroxide cross-linking is highly recommended, as the alkaline environment could cause a sulfur crosslinked elastomer to continue to react, resulting in adverse properties. **Table 1** shows the formulation used. The characteristics of the carbon black N990 differ only very slightly from those of the surface-treated Neuburg Siliceous Earth. The difference in density of 1.8 g/cm^3 to 2.6 g/cm^3 is one of the largest differences here. **Table 2** shows the characteristics of the two fillers. The compounds were subsequently vulcanised at 180 °C in the press. The vulcanisation/conversion time was t_{90} + 10 %.

3.2 Requirements of VW TL 52686

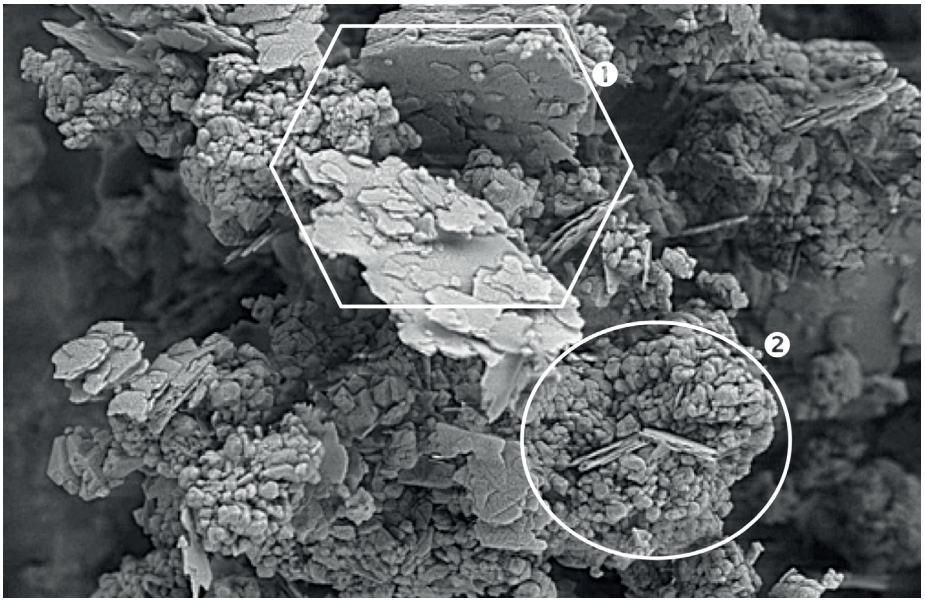
As the requirements for version A (O-ring) and version B (hose liner) are exactly the same, we were fortunately able to offer a common formulation for both injection moulding and extrusion. The hose sheath (also version B) was deliberately not considered, as it does not have to satisfy any specifications with respect to an aqueous urea solution. The test was performed in accordance with DIN using the test parameters from VW TL 52686.

4 Results

4.1 Rheological results

The use of Aktisil VM 56 results in a 20 % increase in the maximum vulcanisation speed. It also leads to a reduction in the conversion time t_{90} by a further 20 %; from 5.6 min with carbon black to 4.7 min with Aktisil VM 56. This should allow the cycle time to be reduced during production.

Fig. 1: SEM image of the Neuburg Siliceous Earth; 1: Lamellar kaolinite; 2: Corpuscular silica



Tab. 1: Formulation used for the experiment

Raw material	Description	phr	phr
Keltan 4450S	Ethylene Propylene Diene Rubber, amorphous, ML 1+4 (125 °C): 42 MU	100	100
Carbon black N990	MT carbon black	120	
Aktisil VM 56	NKE, surface-treated		120
Process oil P460	Paraffinic plasticiser	20	20
Vulkanox HS/LG	TMQ, anti-oxidation agent	1	1
TAC GR 70	Triallyl cyanurate, 70 %, co-activator	1	1
Perkadox 14-40B-pd-s	Di(tert-butylperoxyisopropyl)benzene Peroxide, crosslinking agent	5	5
Total		**247**	**247**

4.2 Mechanical properties

With the same filler addition, the hardness of the compound with Neuburg Siliceous Earth is 65 Shore A, while that of the carbon black-filled blend of 61 Shore A is at the lower limit of the specification. As far as the tensile strength is concerned, both fillers clearly surpass the specification limit of 8 MPa, with the Aktisil VM 56 showing a slightly higher tensile strength (11.7 MPa compared with 10.8 MPa for the carbon black-filled blend) **(fig. 3).** Both fillers also clearly meet the requirements for elongation at break. As far as the modulus is concerned, the use of Aktisil VM 56 led to a significant improvement in performance. This resulted here in a 50 % higher modulus at 100 % elongation, with the carbon black-filled compound only just satisfying the specification of 2.5 MPa (2.8 MPa) **(fig. 4).** As far as the compression set (94 h/23 °C and 22 h/120 °C) is concerned, both compounds return the necessary low measured values.

4.3 Ageing in hot air

The hot air ageing tests were performed over a test duration of 94 h and 504 h, respectively, at a temperature of 120 °C. Both blends were easily able to meet the required specifications and provide more than adequate safety for use at the ele-

Tab. 2: Characteristics of the filler carbon black N990 and Aktisil VM 56

Characteristics		Carbon black N990	Aktisil VM 56
Density	g/cm³	1,8	2,6
Grain size d_{50}	µm		2,2
Grain size d_{97}	µm		10
Screen retention > 40 µm	mg/kg		20
Screen retention 45 µm/325 mesh	ppm	18	
Oil number	g/100g		45
DBP absorption	ml/100 g	38	
Specific surface BET	m²/g		9
CTAB surface	m²/g	7	
Surface treatment		None	Vinyl silane

Fig. 2: Measurements of the vulcanisation speed (in Nm/min) at 180 °C and 0,2° deflection and measurements of the conversion time t_{90} (in min) at 180 °C and 0,2° deflection

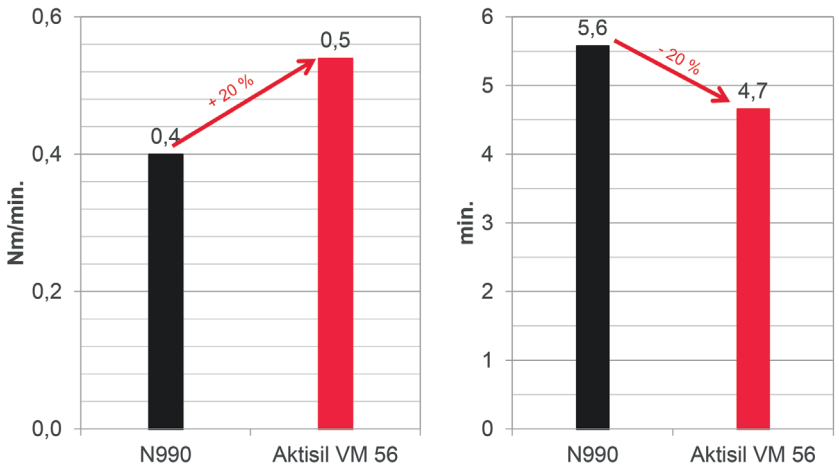
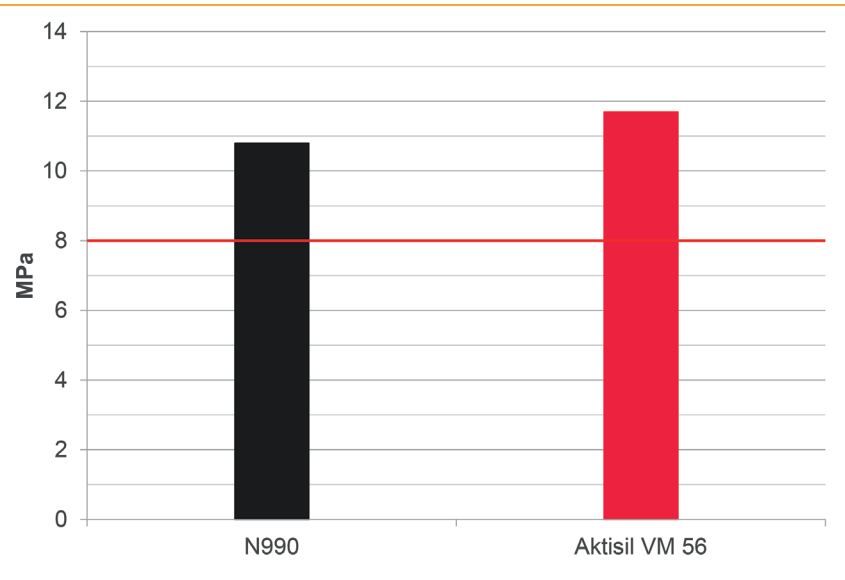


Fig. 3: Results of the measurement of the tensile strength in accordance with DIN 53 504, S2



vated temperature. The change in hardness of the two samples during hot air ageing after 94 h was –1 Shore A (carbon black) and +/– 0 Shore A (Aktisil VM 56). After 504 h, the hardness of the blend with carbon black had not changed, the blend with Aktisil VM 56 showed a change in hardness of +2 Shore A.

4.4 Urea resistance

The storage in urea solution took place at 80 °C, since the hydrolysis reaction with ammonia and water already takes place at this temperature. Both Aktisil VM 56 and the carbon black offer excellent resistance to AdBlue and show no change in hardness and no change in weight after storage **(fig. 5).** The tensile strength and the elongation at break were well clear of the specification limits.

4.5 Blooming

As shown in **figure 6** the compound with the carbon black tends to blooming of decomposition product of the peroxide. This can be seen as a white, crystalline powder on the surface of the test specimens one day after vulcanisation. It can be assumed that this is a di(2-hydroxyisopropyl)benzene, as according to the manufacturer this can be a decomposition product of the "Perkadox 14" peroxide used. Other possible decomposition products, such as diacetylbenzol, can be ruled out, as the melting temperature of this product is below the 120 °C of the hot air ageing and the powder is still visible on the surface after this ageing. Aktisil VM 56 prevents this blooming and hence the soiling of the surface so that one complete work step, the cleaning of the products, can be saved.

4.6 Hose extrusion

The compounds were extruded on a Schwabenthan "Polytest 30 R" laboratory extruder with a take-off speed of 5 m/min. The hose profiles were not vulcanised after extrusion. The exact extrusion parameters can be seen in **table 3.** The dimensions of the hose die (inside diameter: 16.5 mm; outside diameter: 20 mm) result in a nominal wall thickness of 1.75 mm. The advantages of us-

ing Aktisil VM 56 become apparent during processing during the extrusion. The carbon black N990 causes a wavy and uneven surface, while the hose with Aktisil VM 56 has a smooth surface. Furthermore, Aktisil VM 56 results in a higher collapse resistance of the hose profile **(fig. 7).**

4.7 Compound raw material costs

Use of Aktisil VM 56 allows the costs to be considerably reduced. While the costs by weight are reduced by up to 27 %, a cost reduction by volume of 20 % is still achieved, despite the higher density of the Neuburg Siliceous Earth. While the carbon black prices often fluctuate widely, the costs for the Neuburg Siliceous Earth remain calculable with only a minimum increase over time.

5 Summary

The substitution of carbon black N990 with Aktisil VM 56 offers a number of advantages. A higher modulus at 100 % elongation is achieved, as well as a shorter vulcanisation time which results in a reduction in the cycle time. This can be achieved with an absolutely comparable resistance to AdBlue. During extrusion, Aktisil VM 56 exhibits a higher surface quality and a better stability. The Neuburg Siliceous Earth also prevents not only the blooming, eliminating the need for a subsequent cleaning process, but also ensures that the vulcanisates can be processed to produce parts that can be distinguished by colour. Furthermore, the blend costs are reduced significantly by the use of Aktisil VM 56. All these advantages

Fig. 4: Results of the measurement of the modulus with 100 % elongation

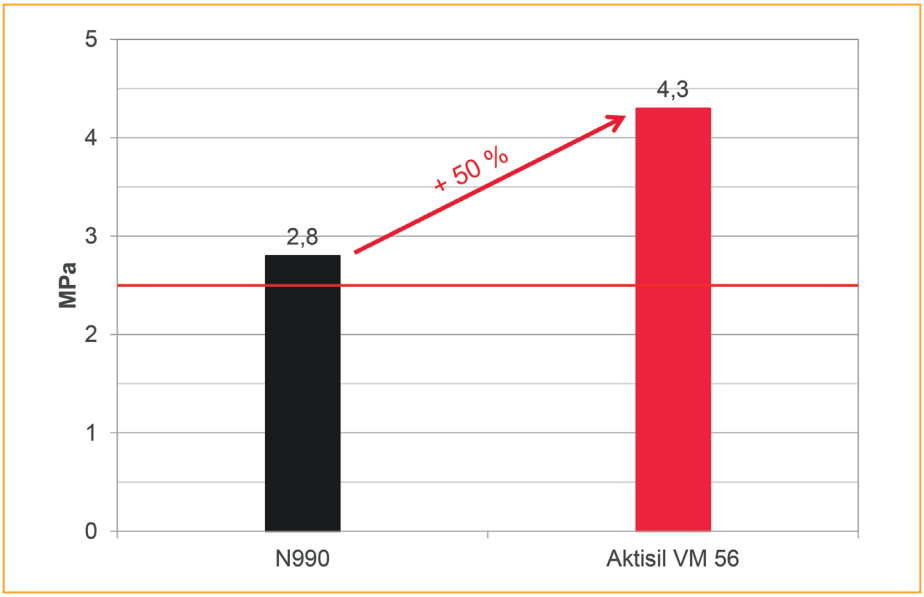


Fig. 5: Change in weight of the blends after storage in urea solution at 80 °C (solid bar: after 94 h; dotted bar: after 504 h). The dotted line shows the specification after 504 h, the solid line the specification after 94 h.

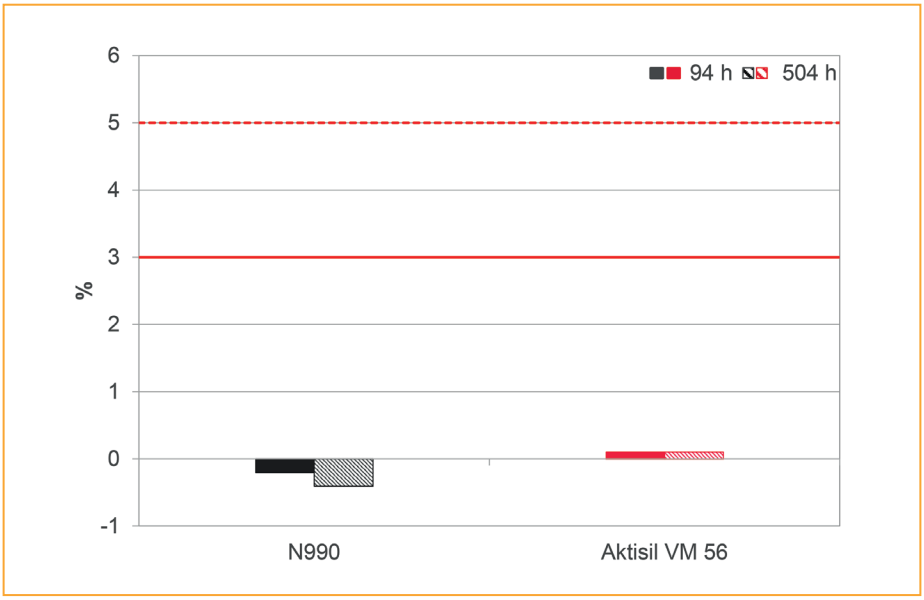
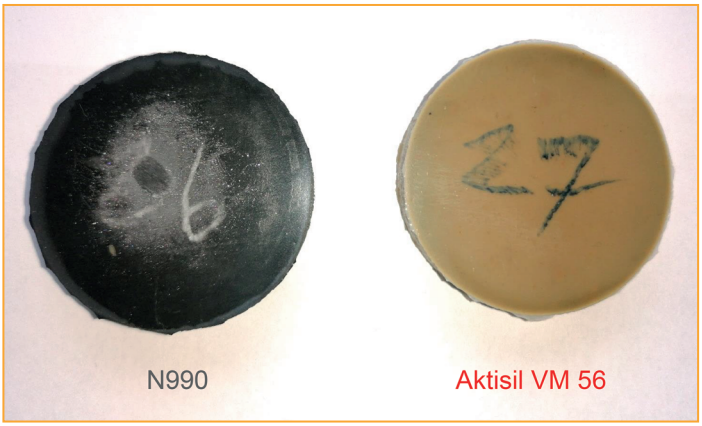


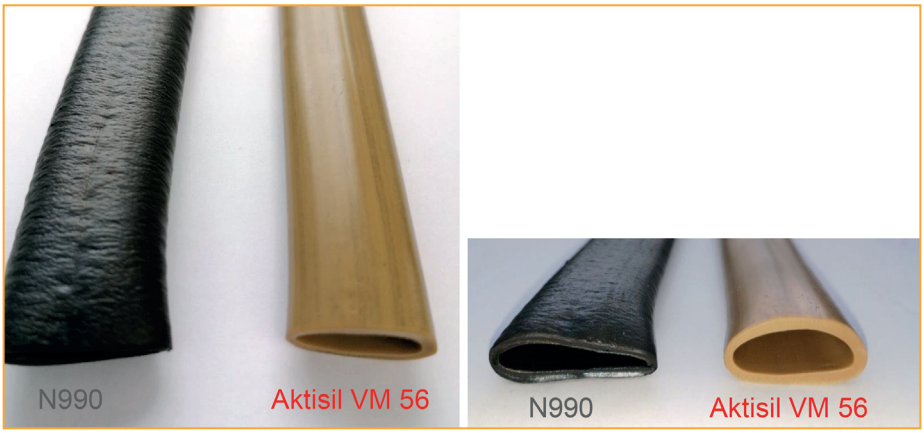
Fig. 6: Blooming



Tab. 3: Parameters of the hose extrusion

Extruder	Schwabenthan Polytest 30 R
Screw diameter	30 mm
Barrel length	450 mm
Temperature setpoint: Head / zone 1 / zone 2	110 °C / 70 °C / 70 °C
Profile	See below
Filler strips	Cold, untreated
Extrusion speed	5 m/min

Fig. 7: Surface quality and stability of the extruded hose profiles at a haul-off speed of 5 m/min



are achieved using Neuburg Siliceous Earth, with 100 % compliance with the specifications of VW TL 52686.

6 References

[1] German Association of the Automotive Industry (Verband der Automobilindustrie e. V.). (No date). Antriebstechnik – Abgastechnik zur Stickoxidreduzierung. https://www.vda.de/de/themen/innovation-und-technik/antriebstechnik/abgastechnik.html (last accessed on 23 February 2021).

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