ls in the automotive industry
N990 with Neuburg

allow further customisation and/or cost optimisation.

1 Introduction

NBR seals are used in a variety of mechanical engineering and automotive industry applications. Corresponding requirements are listed in ASTM D2000. For this purpose, carbon black N990 is often used along with carbon black N550 for rationalizing the property profile inclusive of costs. Depending on the price of the fossil raw materials, carbon black prices are subjected to considerable fluctuations. The long-term trend is clearly going up. The price of mineral fillers is only slightly influenced by fossil raw materials, but rather is only rising marginally without showing fluctuations. There are also temporary supply bottlenecks for carbon black N990, which can be circumvented through the use of fillers based on siliceous earth. In addition, reliable delivery times and high availability can also be ensured for Neuburg Siliceous Earth products. The objective of this study was to replace carbon black N990 available in a typical NBR formulation for oil seals with Neuburg Siliceous Earth, maintain a constant property level and contribute to cost reduction.

2 Experimental

The studies to replace N990 took place using a base formulation in which the available thermal black N990 was replaced with various siliceous earths – both untreated as well as surface treated – in order to be able to determine the resulting property profiles compared to the N990 standard. All details regarding this can be found in the following sections.

2.1 Mixture composition

The formulation used for the tests is listed in **Table 1**. This base formulation represents a molded part formulation for oil seals as they are used in many cases in the automotive industry. The nitrile rubber used has an average content of ACN and is thus suitable for common standard oils. Its Mooney viscosity is also in the middle range. The total carbon black share is 110 phr and consists of 60 phr Corax N550 and 50 phr carbon black N990. The plasticizer content is only 10 phr, which results in a hardness of 70 Shore A with a 1:1 replacement ratio for the thermal back. Aktisil PF 216, Aktifit AM, Silfit Z 91, Sillitin Z 86 and Sillitin N 82 were used as the replacement fillers. Aktisil PF 216 and Aktifit AM are surface treated siliceous earths – PF 216 treated with tetrasulfane silane for functionalization of the filler surface, AM treated with an aminosilane coated Silfit Z 91. Silfit Z 91 is derived from Sillitin Z 86 via a special calcination process and is characterized by low moisture absorption, excellent dispersion behavior and a generally lower compression set than the base product. The other Sillitins being tested were also so-called standard siliceous earths.

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If you look at the characteristic values of the carbon black N990 compared to one of the various siliceous earths, you will find that there are only relatively minor differences apart from the density. The difference in density of 1.8 (N990) to 2.6 g/cm3 (siliceous earths) is naturally considerable and is caused by the origin and composition of the materials. For example, if you look at the sizes of sieve residue, oil absorption and BET/ CTAB surface that are normally used to evaluate the deviations to each other, the deviations are minor to each other in comparison.

An EV system (low sulfur quantities in combination with a high accelerator ratio) was used as the cure system. These kinds of systems improve the thermal stability of the cured rubber material, among other things.

2.2 Compound mixing and curing

All compounds were mixed on a laboratory mill (Schwabenthan Polymix 150 L, Ø 150 x 300 mm) at 20 rpm and a batch size of approx. 500 cm3. The rollers were tempered to 40 °C. The mixing times were adjusted according to the incorporation properties of the fillers and registered, and took approx. 20 min.

Curing was done in an electrically heated press at 170 °C. The cure time was always 5 min, both for the 2 mm sheets as well as the rebound and compression set test samples.

2.3 Testing

As already mentioned, ASTM D2000-08, Material type/ class CH was used as a guideline for the individual tests. ASTM D2000 frequently serves as a classification standard for the specification of rubber parts and O-rings that are used in many cases as sealing elements in contact with oils as well as other media. The polymers most frequently used for the specified requirements are assigned to the material type/class. The identifier “CH” stands for nitrile and epichlorohydrin polymers. Specific base requirements must be maintained depending on the classification/specification. If Grade > 1 is listed, then additional requirements must be fulfilled. Here Grade 2 and Grade 3 were selected with additional requirements for the media resistance (IRM 901, IRM 903, Liquid C), temperature resistance and behavior for heat aging. Table 2 provides an overview of this.

In individual cases, the following test procedures/ standards were used for determining the rheological and mechanical properties of the test mixtures.

- Mooney viscosity ML(1+4) 100 °C as per DIN 53 523, Part 3
- Mooney scorch time ML(+5) 120 °C as per DIN 53523, Part 4
- Maximum cure rate, time of maximum cure rate, loss angle tan d, conversion time t_{90} on the Göttfert elastograph at 170 °C, 0.2° deflection as per DIN 53529-A3
- Hardness Shore A as per DIN 53505
- Tensile strength, elongation at break, modulus 50 % as per DIN 53504, S2 bar
- Tear resistance as per DIN ISO 34-1, strip specimen
- Compression set 22 h / 100 °C as per DIN 53517

3 Results

Only the most important results of the testing will be presented in the following because, nearly as expected, there were no significant deviations in some properties due to the filler replacement – e.g. initial hardness (in the range of 70 ± 5 Shore A), rebound elasticity (identical for all mixtures) or volume change due to immersion in oil IRM 901 after 70 h at 125 °C (only unimportant differences of approx. 1 %).

3.1 Mooney viscosity and Mooney scorch time

If you replace the carbon black N990 with the named siliceous earths, the Mooney viscosity hardly changes and fluctuates between approx. 75 and 82 MU. Carbon black N990 and Aktifit PF 216 were side by side, Aktifit AM and Silfit Z 91 measured a somewhat lower Mooney viscosity compared to thermal black, and Sillitin Z 86 and Sillitin N 82 had a slightly higher viscosity. Therefore, a slightly positive impact on the processing of the mixture is to be expected for AM and Z 91.

Table 1: Tested NBR base formulation 70 Shore A

Ingredient	Description	Quantity in phr
Krynac 2950 F	NBR, 30 % ACN, ML (1+4) 100 °C 53 MU	100
Zinkoxyd aktiv	Zinc oxide	5
Stearic acid	Processing aid	0.5
Agerite Resin D pastilles	Antioxidant	2
Corax N550	FEF carbon black	60
Carbon black N990	MT carbon black	50
Mediaplast NB-4	Ester plasticizer	10
Vulkacit Thiuram/C	Accelerator, TMTD	2.5
Vulkacit CZ/C	Accelerator, CBS	2
Ground sulfur	Curing agent	0.2
Total		232.2

Table 2: Requirements and testing conditions for the test formulation as per ASTM D2000-08, Type CH

Base requirement:
Hardness: 70 ± 5 Shore A
Tensile strength: >10 MPa and/or >14 MPa
Elongation at break: > 250 %
Compression set: < 25 % at 100 °C and 22 h
Grade 2:
Reference liquid IRM 901 70 h / 125 °C
Reference liquid IRM 903 70 h / 125 °C
Reference liquid, Liquid C 70 h / 23 °C
Hot air 70 h / 125 °C
Grade 3:
Reference liquid IRM 901 70 h / 150 °C
Reference liquid IRM 903 70 h / 150 °C
Hot air 70 h / 125 °C

Replacement of carbon black N990

The resulting Mooney scorch times, which represent a measure for the scorching behavior of a mixture during processing, were 12 to 17 min. The reference mixture with N990 was approx. 15 min. With Aktifit AM, Silfit Z 91 and Sillitin Z 86, the scorch times were shorter compared to N990 by 2 – 3 min, but remained in the acceptable range. Aktisil PF 216 and Sillitin N 82 had longer times by 1 – 2 min compared to carbon black and thus delayed the scorching. On the whole, the effects of the filler replacement can be considered to be low.

3.2 Cure characteristics

As **figure 1** makes clear, the maximum cure rate increases considerably with Aktisil PF 216 compared to the mixture with carbon black N990, while the highest value of the cure rate with the remaining siliceous earths drops slightly. The cause for the effect occurring with PF 216 may be due to the surface treatment of this filler with tetrasulfane silane.

In addition, the time of maximum cure rate – compared to the N990 mixture – is also reached significantly more quickly in the mixture with Aktisil PF 216 (**fig. 2**). Here we must also assume that this acceleration effect is due to the silaneization of the filler. In contrast, there was only a modest acceleration with Sillitin Z 86 and Sillitin N 82. The mixtures with Aktifit AM, Silfit Z 91 and carbon black N990 reach their maximum cure rate at the same time and thus do not differ from each other in this property.

The changes in the loss angle tan d resulting from the filler replacement are illustrated in **figure 3** for the various mixtures. Aktifit AM, Silfit Z 91 and Sillitin Z 86 match each other with regards to the tan d. Generally speaking, it is lower than the N990 mixture. For the mixture with Aktisil PF 216, it is even significantly lower and Sillitin N 82 remains on the same level as the pure carbon black mixture. Since the tan d is an indicator for the filler-filler interaction in the compound, it can be assumed that this interaction in the Aktisil mixture is the lowest, followed by Aktifit, Silfit and Z 86, followed by N990 and N 82. The cross connection to the filler structure and the surface treatment is obvious.

Figure 1: Maximum cure rate – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

Nm/min

Figure 2: Time of maximum cure rate – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

min

Figure 3: Loss angle tan δ – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

rad

Figure 4: Tensile strength initial values – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

Requirement: > 10 / > 14

MPa

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The conversion time t_{90} is used as a standard, mixture-typical benchmark for the required full cure time of a rubber article – depending on other ancillary conditions such as the wall thickness of the respective part. It is shorted by approx. 0.5 min by all siliceous earth types listed here compared to thermal black N990, the least by Aktisil PF 216 (approx. 0.4 min) and the most by Sillitin N 82 (approx. 0.5 min). The reduction of the conversion time t_{90} should also enable a reduction of the respective cycle times for regular article production compared to N990.

3.3 Mechanical properties – Initial values

For material type/class CH, there are various requirements for the tensile strength at a hardness level of 70 ± 5 Shore A depending on the application. The tensile strength requirement of >10 MPa is sufficient for a number of applications. This specification is met perfectly in this study by all tested siliceous earth products. However, the mixture containing carbon black N990, as the data show in **figure 4**, is at a significantly higher level at approx. 15.5 MPa. There is a reason why thermal black N990 or similar are frequently used for improving the tensile strength. The N990 mixture thus meets the requirements of the next highest performance level of >14 MPa tensile strength. This performance level should also be met by Aktisil PF 216 because the 14 MPa value is also exceeded with PF 216 and the resulting tensile strength with N990 is nearly reached with approx. 15 MPa. Silfit Z 91 barely clears the 14 MPa hurdle, Sillitin Z 86 remains slightly below it.

The elongation at break increases with all siliceous earth variants and they significantly exceed the performance profile of the standard by a min. of 250 % (**fig. 5**). While the elongation at break of the N990 mixture is exceeded with Aktisil PF 216 by approx. 30 percentage points, it is higher by approx. 100 percentage points for all other products.

As can be seen in **figure 6**, the modulus 50 % is somewhat higher with Aktisil PF 216 than with carbon black N990. You get a slightly less modulus 50 % with the remaining siliceous earth variants and this with a decreasing tendency in the direction of Sillitin N 82.

Figure 5: Elongation at break initial values – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

Requirement: > min. 250

Figure 6: Modulus 50 % initial values – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

MPa

Figure 7: Tear resistance initial values – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

N/mm

Figure 8: Compression set initial values – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

Requirement: max. 25

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Replacement of carbon black N990

The tear resistance increases slightly with the replacement of carbon black N990 with Aktisil PF 216. It increases significantly with the remaining siliceous earth products and the highest with Sillitin type N 82. The individual details can be seen in **figure 7**.

When looking at the compression set, Aktifit AM is again at the same level as the pure carbon black mixture and achieves the best result of all tested siliceous earths variants together with Silfit Z 91. With Sillitin Z 86, Sillitin N 82 and Aktisil PF 216, the compression set increases noticeable, but all results lie safely within the selected performance level of ASTM D2000 and thus under the maximum permitted 25 % compression set (**fig. 8**).

3.4 Grade 2 – Immersion in oil IRM 903 at 125 °C

Oil resistance was tested at 125 °C with the aggressive standard oil IRM 903 as a further property. The hardness decreases in all cases. This hardness drop, however, remains within the limits, reaches a maximum of 5 points Shore A (for Silfit Z 91) and thus remains within the tolerance of ±10 Shore A. Aktisil PF 216 leads to the lowest reduction in hardness and thus the best result. The hardness drop for the remaining mixtures is to the same degree and thus remains exactly on the level of the pure carbon black mixture (**fig. 9**).

3.5 Grade 2 – Immersion in reference liquid C at 23 °C

In addition to the immersion in oils IRM 901 and IRM 903, the resistance against automotive fuel was also tested for the various mixtures. Liquid C served as the reference as per ASTM D471. The testing took place according to ISO 1817:2011 for 70 h at 23 °C. The individual results for the hardness change are summarized in **figure 10**. On an overall basis, the hardness reduction did not exceed 20 points Shore A (Sillitin Z 86 and Sillitin N 82) and thus remained significantly within the tolerance ranges of 0/-30 Shore A required for a decrease in hardness. Once again, the hardness with Aktisil PF 216 decreases significantly less here than with carbon black N990. The mixture with Aktifit AM also decreased less than the N990 mixture. Silfit Z 91 was on the same level with the thermal black.

3.6 Grade 3 – Immersion in oil IRM 903 at 150 °C

The testing as per Grade 3 requirements represents an additional tightening of the requirements because the immersion is conducted at an increased temperature. The data for oil resistance to – as already stated – the well known aggressively reacting standard oil IRM 903 at 150 °C are thus presented here. The mixture with Aktisil PF 216 again leads to a significantly lower hardness changes as the one with carbon black N990. Sillitin N 82 is also lower than thermal black, Aktifit AM and Sillitin Z 86 are on the same level, Silfit Z 91 results in the greatest hardness change. However, all mixtures easily fulfill the requirements of the standard that tolerates ±10 Shore A (**fig. 11**).

Figure 9:

Hardness change after 70 h immersion in oil IRM 903 at 125 °C – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

Requirement: ±10

Shore A

Figure 10: Hardness change after 70 h immersion in liquid C at 23 °C – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

Requirement: 0/-30

Shore A

Figure 11: Hardness change after 70 h immersion in oil IRM 903 at 150 °C – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

Requirement: ±10

Shore A

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In addition to the hardness, the results of the swelling behavior of the mixtures can also be discussed. The data are shown graphically in **figure 12**. Generally speaking, Aktisil PF 216 triggers a lower volume increase than carbon black N990. The volume changes with the remaining siliceous earths are only marginally higher than the increase for the pure carbon black mixture, showing no significant differences between the products. With regards to the fulfillment of standard requirements, all tested mixtures are easily in the permitted tolerance range of 0/+25 % because 11 % of swelling is not exceeded for all.

3.7 Cost aspects

As is shown in figure 13, the use of siliceous earth products results in a significant reduction in mixture raw material costs. This is all the more remarkable because the different mixture densities compared to the mixture with carbon black N990 have already been taken into account in the volume-related mixture price indices listed. Thus, there is a cost savings of approx. 4 or 6 % with Aktifit AM and Silfit Z 91. Even more pronounced, you can achieve a cost savings of up to 9 % with Sillitin Z 86 and Sillitin N 82. Even Aktisil PF 216 results in a small price advantage.

4 Conclusion

Aktisil PF 216 results in a lower hardness change along with improved cure characteristics (t_{90}, loss angle tan d) and the same high tensile strength after immersion in oil IRM 903 and fuel Liquid C when compared to carbon black N990.

A good compression set and no mold fouling characterize the effect of Aktifit AM and Silfit Z 91 at a cost savings of approx. 4 or 6 %.

Both Sillitin Z 86 and Sillitin N 82 can achieve a cost reduction of up to 9 % with minimum value changes.

A combination of Sillitin and Aktisil PF 216 offers a way to balance out the physical properties and the cost situation. Thus a 50:50 combination, for example, achieves a property profile that tends to be more like that of Aktisil PF 216.

High availability and a reliable supply of siliceous earth products are additional important arguments in favor of this.

The end result is that carbon black N990 can be replaced with Aktisil PF 216 with technical advantages and in particular, replaced with other siliceous earth products with a cost reduction.

Figure 12: Volume change after 70 h immersion in oil IRM 903 at 150 °C – Comparing carbon black N990 with siliceous earths

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

Requirement: 0/+25

Figure 13: Cost aspects – Comparing carbon black N990 with siliceous earths based on the mixture liter price (as of: Price situation Germany 01/2015)

Carbon black N990

Aktisil PF 216

Aktifit AM

Silfit Z 91

Sillitin Z 86

Sillitin N 82

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