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Heat-conductive, flame-retardant silicones

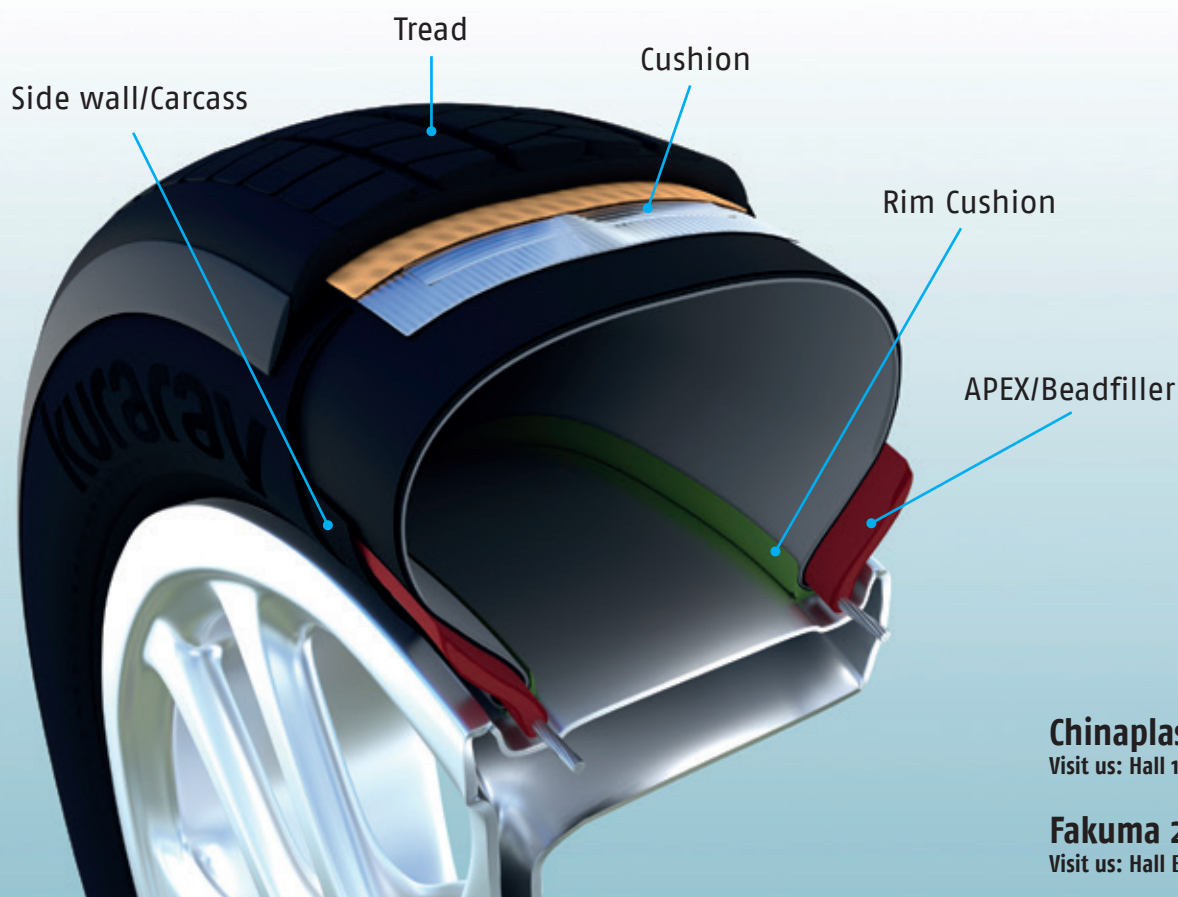
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Silicone elastomers with heat conductivity or flame retardant characteristics

K. Lehmann, A. Nawracala

The following article discusses the use of novel compounds of the Tegosil series, which are intended to significantly increase the thermal conductivity of HCR and even LSR based silicone elastomers or – by adding such compounds – improve the flame retardant properties in an easy way. Heat transfer characteristics from hot disk testing are presented and the reduced burning time in the UL 94 evaluation illustrates the improved flame resistance of the resulting elastomer formulations.

1 Introduction

Silicone elastomers are materials that offer high heat resistance in comparison to other elastomers. A previous article explained how this characteristic can even be improved distinctly through the use of additives of the Tegosil series, with an addition of 2–4 % in HCR and even in LSR. This article will explain how the heat conductivity characteristics of silicone elastomers can be improved and how enhanced flame retardancy can be achieved, while using up to 70 % of novel Tegosil compounds.

In general, the user can purchase fully formulated HCR silicones with a flame retardancy classification, whereas the free formulator often has problems dispersing large amounts of inorganic fillers that are important for both characteristics – flame retar-

dancy and heat conductivity. In fact, for LSR materials, it is far more difficult to achieve these characteristics, because the use of additional significant amounts of filler in addition to the silica, which is indispensable for the mechanics of the system, very quickly leads to viscosities that are so high that the LSR can no longer be processed. In addition, the LSR processor has no equipment that can disperse fillers or handle powder materials at all.

The following article illustrates how new types of compounds from the Tegosil series can be used to achieve silicone elastomers that have good mechanical properties and also display high heat conductivity or flame retardancy.

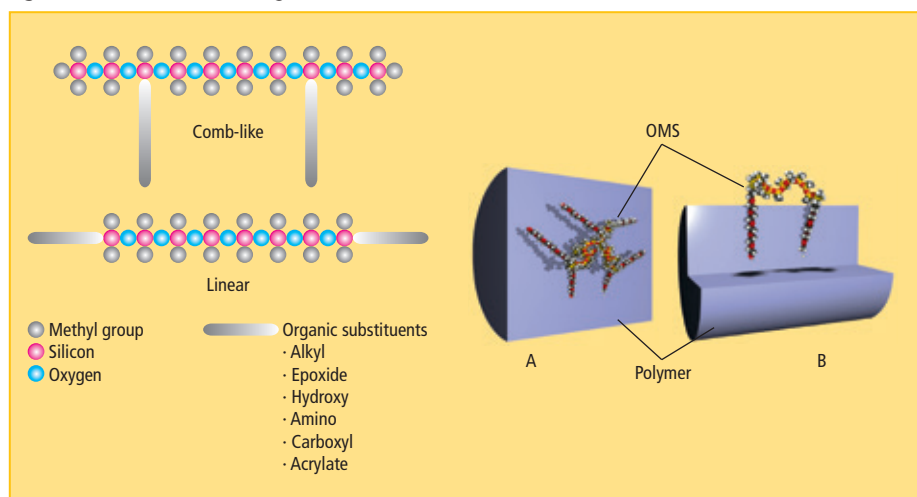
Evonik Nutrition & Care develops specialty chemicals on the basis of a wide variety

of technologies, with the so-called organo-modified siloxanes (OMS) playing an important role. Organomodified siloxanes are additives that are already being used in a variety of thermoplastic materials and in rubber formulations, either directly as process aid or to enhance performance, for instance to improve mechanical properties, to modify the haptics (reduced stickiness), or even to reduce the coefficient of friction (COF). If the OMS technology is designed appropriately, however, these structures also display an ability to act as dispersing agents. It is driven by their orientation on pigment and filler surfaces of different surface energy, thus reducing it. Such additives can be used either directly during dispersion in the silicone rubber, or they can be used for prior surface treatment of the materials to be dispersed. In addition to the dispersing effect, this also leads to compatibilization of the surrounding matrix, so that distinctly improved mechanical properties are often observed, and a lowering of viscosity often permits an increase in the filler content. These characteristics of OMS technology were optimized for the development of the new Tegosil products and are now being used in Tegosil HT and Tegosil FR.

2 Organomodified siloxanes and their structure

To give the reader a better understanding, **figure 1** illustrates the general structure of organomodified siloxanes, as they are available for a wide range of applications from Evonik Nutrition & Care.

Fig. 1: General structure of organomodified siloxanes (OMS)



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

3 Heat conductivity

3.1 Examination of heat conductivity

The compounds developed in the Tegosil HT series can be blended with HCR silicones in any ratio. Typically, a percentage of 40–70 % is required in order to achieve significant effects in improving heat conductivity. The compounds can be used both for platinum-crosslinked HCRs as well as for

the classic HCR materials crosslinked using peroxide.

Actually, Tegosil HT compounds can also be used for LSR elastomers. However, the A and B components of the formulation must be adjusted differently, so that there is no significant influence on the mechanical properties. The reason for this is the continuous phase used in the compounds. Therefore, the crosslinking ratio must be

adjusted differently for the A and B components. Since many LSR processors have neither the corresponding know-how for formulation nor the ability to do the mixing internally, Evonik Nutrition & Care has developed this and will provide assistance in the development.

Figure 2 illustrates applications in which heat conductivity is a desirable characteristic, for instance electronic bedding materials used in making LEDs, underfloor heating systems, seals, and O-rings for various industrial applications. These are mostly HCR applications, because LSR systems with the characteristic of heat conductivity and a viscosity that is low enough for the injection molding process are generally not even available yet.

The heat conductivity of materials can be examined using various methods, such as the laser flash method or the hot disk method. The latter was used in generating the values set out in this article, and comparative measurements with the laser flash method resulted in good agreement. **Figure 3** shows the measurement method used, based on ISO 22007-2.

The HCR test specimens used for the determination of heat conductivity were prepared according to the procedure shown in **figure 4**.

After mixing Tegosil HT into the components A and B of a 50 Shore A LSR and corresponding formulation adjustment, the LSR plates for heat conductivity testing were prepared on an injection molding machine from Engel with a 2K dosing unit from Elmet (**fig. 5**).

Fig. 4: Typical production of an HCR material for the testing of heat conductivity

- Used HCR: Xiameter RBB 2100-50
- Incorporation of Tegosil HT on a double roll mill
- Molded plates in a press for 5 min at 116 °C, with a layer thickness of 2 mm
- Post curing for 4 h at 200 °C
- Specimen cut out
- Evaluation of mechanical data:
 - Hardness in Shore A
 - Tensile strength
 - Elongation at break
 - Tear strength
- Evaluation of heat conductivity

Fig. 2: HCR applications with heat conductivity

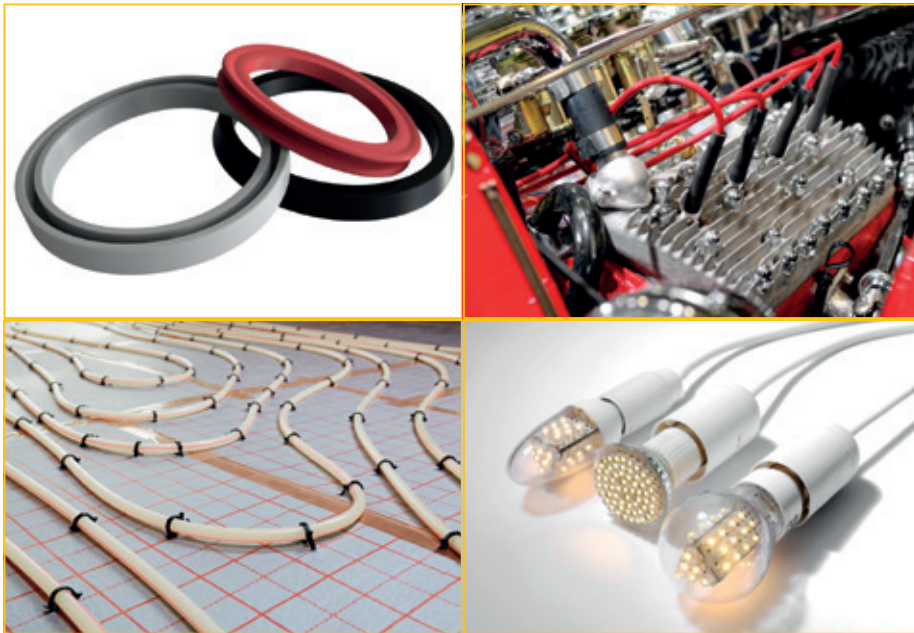
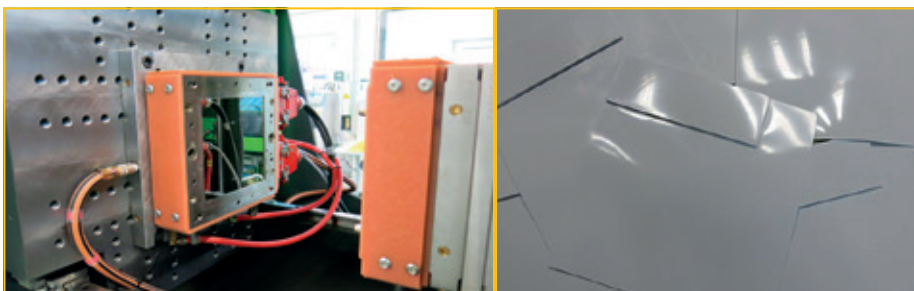


Fig. 3: Material holder and sensor for the hot disk method (heat conductivity measurement)



Fig. 5: Injection molding tool and the test plates produced with it (2 mm and 6 mm thickness)



3.2 HCR and LSR results with Tegosil HT

As mentioned above, improving the heat conductivity of materials often requires a very high content of fillers, including the use of zinc oxide or aluminum oxide. From the extensive investigations of different particles, only those which led to the development of the Tegosil HT products are discussed below. This is done to illustrate that the products of the Tegosil HT series are also of interest to HCR formulators, who can handle dust-producing and powdered fillers and not just for companies, which can only process liquid or highly viscous materials, but not powders.

Figure 6 illustrates the results for a 50 Shore A HCR using 70 % Tegosil HT 2000 (basis Particle 1) and 70 % Tegosil HT 2100 (basis Particle 2). In comparison to this, corresponding equivalent amounts of powdered Particles 1 and 2 were mixed into the 50 Shore A HCR, as they are added from the Tegosil HT compounds equivalently.

Starting from a 50 Shore A HCR, which – with an elongation at break of 600 %, a tensile strength of 10 MPa, and a tear strength of 26 N/mm – can be viewed as the standard system, it becomes clear that both particles lead to a serious change in mechanical properties. In comparison to this, even Tegosil HT 2000 and HT 2100 show a moderate change in mechanical properties and do so at the highest possible filler content with 70 % compound use. Assuming that a lower percentage can be used for many applications or that the formulator can adjust the reduced tensile strength and tear strength, the potential can be seen even for sealing parts. Furthermore, in applications that are rather static, meaning non-moving, these properties are already acceptable at this level.

Table 1 shows the corresponding heat conductivity values, measured with the hot disk method at room temperature and at 100 °C, because the applications mentioned in section 3.1 often require this profile of characteristics not just at ambient temperature but also at elevated temperatures. Since heat conductivity is a temperature-dependent material constant, it must be determined

relative to temperature. For instance, in under-hood application close to the motor, the functional temperature of components is often important, e.g. 120 °C for a seal, so that the heat conductivity at this temperature is relevant. By dissipating the resulting heat, it may be possible to retain the mechanics of the component longer, reduce functional faults, and thus extend the service life of the part further, possibly in combination with the Tegosil Heatban series.

The values show clearly that the addition of 70 % of the two Tegosil HT products can more than double the heat conductivity, starting from 0.24 W/(m·K). This is also possible at an elevated temperature of 100 °C and not just at room temperature. In principle, this is also possible by dispersing the fillers in the HCR base. However, in combination with the examination of the mechanical properties, it becomes clear why even for formulators who can do this, the

Tab. 1:
Heat conductivity of an
HCR elastomer

| | Thermal conductivity in W/(m·K) | |
|--|---------------------------------|--------|
| | Room temperature | 100 °C |
| Without Tegosil HT | 0.24 | 0.23 |
| % Particle 1 equivalent to Tegosil HT 2000 | 0.57 | 0.51 |
| 70 % Tegosil HT 2000 | 0.56 | 0.51 |
| % Particle 2 equivalent to Tegosil HT 2100 | 0.63 | 0.57 |
| 70 % Tegosil HT 2100 | 0.63 | 0.58 |

Fig. 6: Mechanical properties of an HCR material – heat conductivity modified with Tegosil HT 2000 and 2100 compared to Particle 1 and 2, respectively

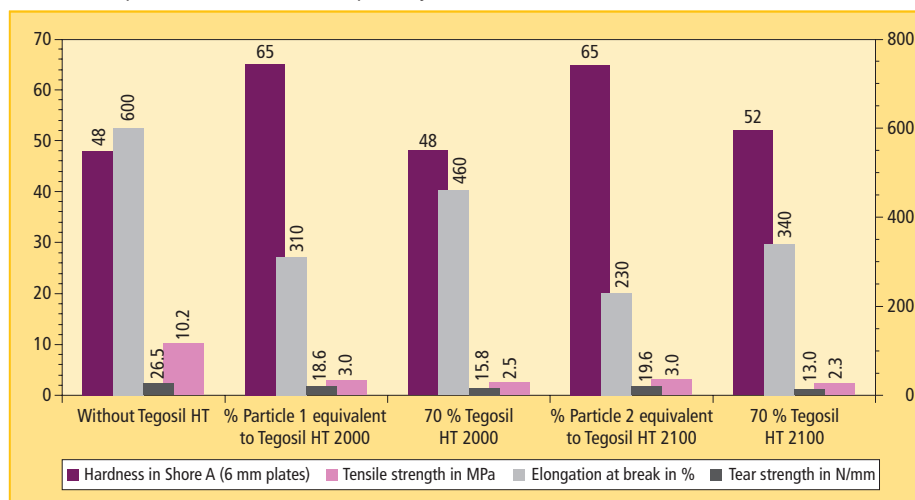
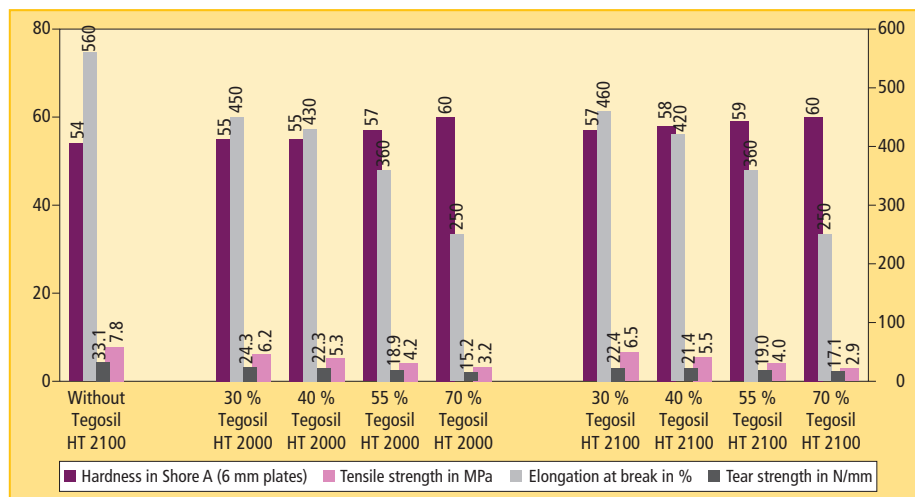


Fig. 7: Mechanical properties of a 50 Shore A LSR depending on the content of Tegosil HT products



new pasty Tegosil HT products are attractive, not to mention the distinctly reduced

mixing times that can be achieved in this way.

Tab. 2: Heat conductivity in HCR with different percentages of Tegosil HT 2100

| Mechanical properties | | | | | Thermal conductivity in W/(m·K) | | | | | |
|-----------------------|-----------------------------------|-------------------------|-----------------------|--------------------------|---------------------------------|-------|-------|--------|--------|--------|
| Xiameter RBB 2100-50 | Hardness in Shore A (6 mm plates) | Tensile strength in MPa | Tear strength in N/mm | Elongation at break in % | RT | 50 °C | 75 °C | 100 °C | 125 °C | 150 °C |
| 0 % HT 2100 | 48 | 10.2 | 26.5 | 600 | 0.24 | 0.24 | 0.24 | 0.23 | 0.23 | 0.22 |
| 40 % HT 2100 | 54 | 5.2 | 22.5 | 510 | 0.37 | 0.37 | 0.37 | 0.35 | 0.34 | 0.32 |
| 55 % HT 2100 | 55 | 3.8 | 20.1 | 460 | 0.46 | 0.45 | 0.44 | 0.42 | 0.40 | 0.39 |
| 70 % HT 2100 | 55 | 2.4 | 15.8 | 360 | 0.63 | 0.61 | 0.60 | 0.58 | 0.55 | 0.51 |

Tab. 3: Heat conductivity of an LSR

| | Thermal conductivity in W/(m·K) | | | | | |
|----------------------|---------------------------------|-------|-------|--------|--------|--------|
| | RT | 50 °C | 75 °C | 100 °C | 125 °C | 150 °C |
| Without Tegosil HT | 0.23 | 0.26 | 0.24 | 0.24 | 0.24 | 0.23 |
| 30 % Tegosil HT 2000 | 0.31 | 0.33 | 0.32 | 0.31 | 0.31 | 0.30 |
| 40 % Tegosil HT 2000 | 0.36 | 0.38 | 0.36 | 0.35 | 0.34 | 0.34 |
| 55 % Tegosil HT 2000 | 0.44 | 0.47 | 0.43 | 0.42 | 0.40 | 0.39 |
| 70 % Tegosil HT 2000 | 0.54 | 0.56 | 0.54 | 0.52 | 0.50 | 0.47 |
| 30 % Tegosil HT 2100 | 0.33 | 0.33 | 0.33 | 0.32 | 0.31 | 0.30 |
| 40 % Tegosil HT 2100 | 0.39 | 0.38 | 0.37 | 0.36 | 0.35 | 0.34 |
| 55 % Tegosil HT 2100 | 0.47 | 0.46 | 0.44 | 0.43 | 0.41 | 0.40 |
| 70 % Tegosil HT 2100 | 0.56 | 0.57 | 0.55 | 0.53 | 0.51 | 0.49 |

Fig. 9: Flame retardancy test and burned HCR



Fig. 10: Transportation as an application with flame retardancy requirements



Table 2 shows mechanical property data and the heat conductivity for another HCR base with different percentages of Tegosil HT 2100 added. From this it can be seen that adding just 40 % Tegosil HT 2100 increases the heat conductivity by 50 %. Adding 55 % Tegosil HT 2100 even makes it possible to double the heat conductivity. This is offset by moderate losses in mechanics, so that this system could be used directly without any further reformulation for a number of applications.

The following discussion deals with the results of using Tegosil HT in an LSR elastomer. The testing used an Elastosil LSR with a hardness of 50 Shore A, 560 % elongation at break, 8 MPa tensile strength, and a tear strength of 33 N/mm. The two compounds were added at 30 %, 40 %, 55 %, and 70 %, while adjusting components A and B of the original LSR. The resulting mechanical property data can be seen in **figure 7**, and the corresponding heat conductivity values are listed in **table 3**.

Generally, the Tegosil HT compounds influence the viscosity of the LSR materials as follows: If low viscosity LSR materials in the range of 20,000 – 80,000 mPa·s are used, the viscosity rises to a maximum of 100,000 mPa·s; if LSR materials with distinctly more than 100,000 mPa·s are used, the viscosity generally drops. The application shown in the example here uses a highly viscous LSR, which became even easier to use on the injection molding machine through the addition of the Tegosil HT compounds.

It becomes clear that the addition of 30 – 55 % can produce interesting LSR sys-

Fig. 8: Typical production of an HCR material for the testing of flame retardancy

- Used material: HCR (Elastosil R 401/50)
- Incorporation of Tegosil FR 1000 and 1,5 % DCIBP (Di-(2,4-dichlorobenzoyl)-peroxide) with the double roll mill
- Molded plates in a press for 10 min at 135 °C, with a layer thickness of 2 mm
- Post curing for 4 h at 200 °C
- Specimen cut out
- Evaluation of mechanical properties:
 - Hardness in Shore A
 - Tensile strength
 - Elongation at break
 - Tear strength
- Evaluation of flame retardancy according to UL 94

tems, whereas the addition of 70 % Tegosil HT compound means that the LSR must either be reformulated or must be used in applications such as casting compounds, where mechanical properties play a lesser role.

4 Flame retardancy

4.1 Examination of flame retardant characteristics

The HCR test specimens needed for the determination of flame retardant characteristics were prepared using the procedure shown in **figure 8**.

For testing the flame retardancy of the HCR elastomers an examination was carried out according to UL 94, although other tests may also be necessary depending on the end application. **Figure 9** shows the equipment used and the HCR elastomer destroyed by the flames.

Particularly in the construction sector and in transport applications, where reinforced or non-reinforced elastomers can be used, flame-retardant silicones can be of greater importance, as shown by the examples in **figure 10**.

4.2 HCR and LSR results with Tegosil FR

35 %, 55 %, and 70 % Tegosil FR 1000 were mixed into a 50 Shore A HCR material in order to determine the extent to which the flame retardancy of the system can be improved. The resulting mechanical characteristics of the system can be found in **table 4**.

Despite the addition of large amounts of flame retardant, there is no stiffening of the HCR, as can often be observed when powdered fillers are added. Looking at the UL 94 test with the burned test specimens as documented in **figure 11**, the HCR compound being tested already shows a distinct reduction in burning duration at an addition of 55 %. This can be achieved in another HCR compound only after addition of 70 % Tegosil FR 1000. Therefore, selecting the compound for which flame retardancy can be

achieved with a lower amount of additive also means that less reformulation work is required to adjust the mechanical properties.

The following section deals with the possibilities of using Tegosil FR 1000 in LSR materials. The remarks on the influence of the material on the viscosity of the LSR system as already explained for Tegosil HT also apply

analogously here – a slight rise for low viscosity LSR and a reduction in viscosity for highly viscous LSR.

Figure 12 shows the mechanical properties data for the 50 Shore A LSR material used; with addition of 40 %, 55 %, and 70 % Tegosil FR 1000 and adjustment of components A and B, in order to balance

Tab. 4: Mechanical properties of an HCR Shore A 50 with Tegosil FR

| | Mechanical properties | | | |
|--|-----------------------------------|-----------------------|-------------------------|--------------------------|
| | Hardness in Shore A (6 mm plates) | Tear strength in N/mm | Tensile strength in MPa | Elongation at break in % |
| Elastosil R 401/50 without Tegosil FR 1000 | 46 | 31.1 | 10.5 | 620 |
| 35 % Tegosil FR 1000 | 48 | 20.8 | 5.3 | 390 |
| 55 % Tegosil FR 1000 | 50 | 18.6 | 4.2 | 340 |
| 70 % Tegosil FR 1000 | 51 | 14.1 | 3.2 | 270 |

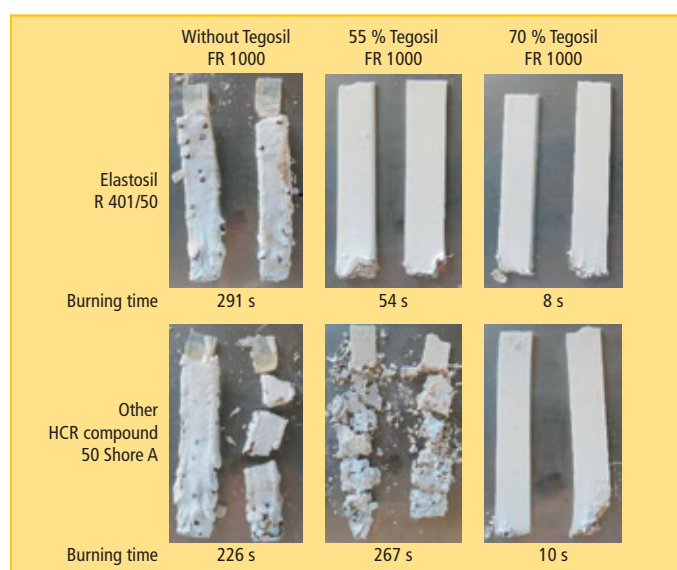
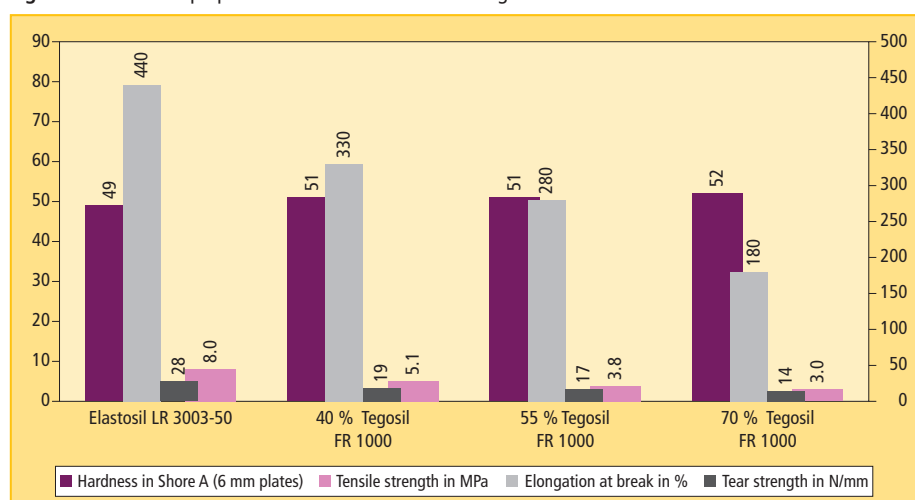


Fig. 11: Flame retardancy of two 50 Shore A HCR compounds

Fig. 12: Mechanical properties of a 50 Shore A LSR with Tegosil FR 1000



the crosslinking accordingly. Together with **figure 13**, which illustrates the burning duration of the test specimens, it quickly becomes clear that even the addition of 40 % Tegosil FR 1000 is enough to achieve flame retardancy. Since the burning duration is 5 s, it may be possible to add less flame retardant compound and thus to further optimize the mechanical properties, especially since

the UL 94 V0 classification has already been achieved here, which, however, is not required in every application.

5 Summary and outlook

The present article explained how heat conductivity can be increased by 50 – 150 %

in both HCR and LSR materials, thus expanding the range of applications for silicone elastomers, without necessitating the handling of large quantities of powdered fillers. The Tegosil HT 2000 and Tegosil HT 2100 compounds used for this purpose are products in paste form, which can be mixed easily with an HCR at any ratio and, in LSR, were mixed proportionately with the A and B components while adjusting the crosslinking. 55 % addition of the heat conductivity compound to HCR or LSR proved to be a percentage with distinctly increased heat conductivity and balanced mechanical property values.

Regarding flame retardancy, this article presented Tegosil FR 1000 at an addition level of 55 % in HCR materials and 40 % in LSR materials (with adjustment of the A and B components) as an easily dosable pasty compound.

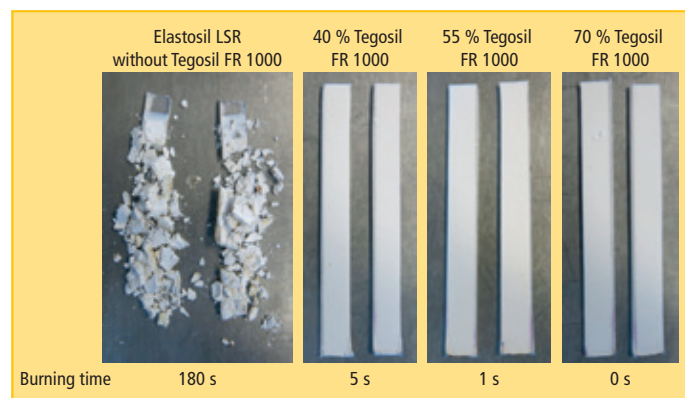


Fig. 13:
Flame retardancy of a
50 Shore A LSR with
Tegosil FR 1000

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