Determination of the Thermal Diffusivity and Thermal Conductivity on Rubbers by means of Light/Laser Flash Analysis (LFA)

Many things we encounter in daily life are made of rubber: tires, hoses, seals, cable sheathings, rubber gloves or shoe soles. All these goods are based on wide-meshed cross-linked polymers with rubberlike properties.

However, which material is the best for a specific application? How can the corresponding production process be optimized? Questions like these are frequent key issues of researchers and engineers. Facing these challenges is often not possible without profound knowledge of two basic thermal properties: the thermal diffusivity and thermal conductivity. For example, the temperature distribution in a tire under service conditions strongly depends on its thermal transport properties. Whereas thermal conductivity is a measure for the amount of heat which is transported from A to B along a temperature gradient, thermal diffusivity specifies how fast the temperature of a material changes.

A precise, reliable and, at the same time, elegant solution to investigate thermal transport phenomena is the light or laser flash method. For a comprehensive material characterization, however, further thermal analysis techniques, such as DSC (differential scanning calorimetry), TGA (thermogravimetric analysis), DMA (dynamic-mechanical analysis, especially with high forces up to the kN range), TMA (thermomechanical analysis) or coupling methods are widely used to investigate elastomer raw materials, semi-finished products or finished parts.

Light/Laser Flash – An Efficient and Reliable Method to Determine Thermophysical Properties

A short energy pulse (from a Xenon lamp or a laser as irradiation source) heats the front side of a plane-parallel sample. An IR detector measures the resulting temperature increase on the sample’s back side (see Figure 1). After applying an appropriate mathematical model to fit the temperature signal data, the thermal diffusivity can be calculated. Additio-
LFA is a non-destructive and absolute testing method. $\Delta T$ is generally small and therefore, the pulse energy is limited. Samples can afterwards be used for further analytical tests, if desired. As the primary signal is the temperature change and not the absolute temperature, the LFA technique does not need to be calibrated.

Altogether, the LFA method is suitable for materials with thermal diffusivity values between 0.01 mm$^2$/s and 1000 mm$^2$/s, which corresponds to thermal conductivity values between 0.1 W/mK and 2000 W/mK thus representing a wide range from insulating materials to diamonds.

**LFA Instrumentation and Experimental Setup**

The application examples discussed in the following sections were measured using a light flash as well as a laser flash system, represented in Figure 3 by the LFA 467 HyperFlash® and LFA 457 MicroFlash®. The LFA 467 HyperFlash® is a light flash system with a Xenon lamp, featuring a pulse energy up to 10 J per pulse; the LFA 457 MicroFlash® is a laser flash system including an Nd:glass laser with a maximum pulse energy of 18 J.

Experiments based on reference materials with ideal sample geometries and ideal behavior reveal that the accuracy of the thermal diffusivity determination is ± 1.5% – as average for a wide range of tests – and of the specific heat capacity determination (where feasible) ± 5% and thus just a little bit higher than typically specified for DSC.

Depending on the instrument type and specimen size, up to 16 samples (LFA 467 HyperFlash®) can be measured in one run within a temperature range dedicated to rubber testing, starting from -100 °C (LFA 467 HyperFlash®) or even -125 °C (LFA 457 MicroFlash®) to 500 °C. Both instruments are equipped with user-friendly software packages each containing a minimum of 15 different models for signal evaluation and a minimum of 3 different procedures for baseline correction.

Thanks to the ultra-fast sampling rate of up to 2 MHz (LFA 467 HyperFlash®) and the patented pulse mapping (Patent no.: US7038209, US20040079886, DE 10242741) which compensates the effects of a finite pulse width, it is also possible to measure thin polymer foils (down to approx. 30 μm).

The used samples had standard geometries with diameters of 12.7 mm and a typical height of 1 to 2 mm. All samples were additionally coated with graphite, even the black ones, to ensure identical experimental conditions. For other sample consistencies and geometries, further sample holders are available.

The low-temperature LFA experiment was conducted under inert conditions to avoid condensation of humidity from the environment. The test runs at room temperature were carried out in a static air atmosphere. The low-temperature $c_p$ determination was performed by means of a DSC.

**Thermal Behavior of a Filled NR/BR Mixture**

Figure 4 shows the thermal diffusivity, specific heat capacity and thermal conductivity data of a filled compound made of natural rubber and butadiene rubber. Due to the discontinuous measurement principle of LFA experiments (stepwise heating/cooling to the desired temperature levels), the graphs consist of distinct measurement points (mean values out of typically 3 to 5 individual results) connected by spline function.
The thermal diffusivity curve (red dots) which starts at a value of approx. 0.32 mm²/s at -125 °C exhibits a step downwards between -75 °C and -50 °C, ending at a level of about 0.18 mm²/s (at -50 °C). This step is related to the glass transition of the rubber mixture and is mirrored in the c_p curve (black triangles) as well. The c_p data varies between approx. 0.65 J/gK at -125 °C and roughly 1.7 J/gK at 80 °C.

The calculated thermal conductivity, however, does not comprise any step, it just shows an almost linear dependence on temperature, starting at approx. 0.2 W/mK at -125 °C and rising up to about 0.3 W/mK at 80 °C. The slight increase in thermal conductivity versus temperature is typical for amorphous materials.

**Carbon Black Content in Natural Rubber**

The thermal diffusivity and thus the thermal conductivity of carbon black is much higher than that of the polymer matrix. For example, graphite has a thermal conductivity of 119 to 165 W/mK at 20 °C, whereas the thermal conductivity of a standard rubber is less than 0.2 W/mK [4], nearly a factor of 1000 lower. Therefore, even small variations in the carbon black content can be registered by the changing thermophysical property values of the sample material.

The presentation in figure 5 depicts the base polymer (natural rubber) mixed with carbon black contents of approx. 19.5 wt%, 22 wt%, 24.5 wt%, 26.5 wt% and ca. 29 wt%, measured at room temperature. The plot reveals an almost linear relationship between the thermal diffusivity and carbon black content, starting at about 0.136 mm²/s for the sample containing 19.5 wt% of carbon black and ending with approx. 0.164 mm²/s for a carbon black content of 29 wt%.

**Conclusion**

Since its introduction in the early 1960’s by Parker et al. [1], the light/laser flash method has become increasingly important for determination of the thermal diffusivity and thermal conductivity in many branches. For several years, there has been an increasing interest also in the polymer field, since thermal conductivity is often used as an input parameter for simulations. Easy sample preparation, fast measurement times and high accuracy are only some of the advantages of this non-contact measurement technique.

Due to the great variety of sample holders, vulcanized and unvulcanised rubbers can be measured. In case of homogeneous solid (vulcanized) samples, it is possible to determine the specific heat capacity in one run together with the thermal diffusivity measurement. For c_p calculations, the signal height of the sample is related to the signal height of a known reference material.

LFA is very sensitive to filler contents, regardless of whether the rubber is mixed with ceramic fillers or, as shown in one of the examples above, carbon black. Here, the thermal diffusivity is clearly dominated by the carbon black and can therefore be directly adjusted by the filler content.

This demonstrates that light or laser flash analysis is a powerful tool to characterize rubber materials not only in terms of their thermophysical properties but also in terms of their composition.

**Literature:**