Average Curve and *SuperPosition* of Curves

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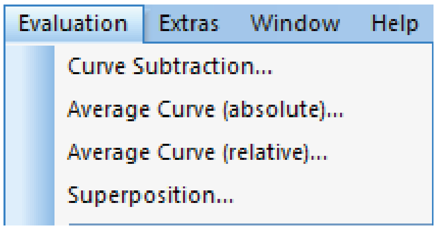
In *Proteus*® analysis version 8.0 or higher, the new Average Curve (absolute), Average Curve (relative) and *SuperPosition* functions are available for DSC, c_p and TGA signal types. They can be accessed via the Evaluation menu depicted in figure 1.



1 Evaluation menu (partial view) of *Proteus*® analysis version 8.0

The purpose of both Absolute Curve (absolute) and Absolute Curve (relative) functions is the averaging of several individual measurements. This leads to an improvement of the signal-to-noise ratio and furthermore to an averaging over the entire sample material measured, which might be inhomogeneous, revealing a more representative result.

It must be emphasized that both Average Curve (absolute) and Average Curve (relative) are only useful if the individual measurement curves were done on the same sample material under the same measurement conditions (heating rate, crucible, gas atmosphere).

Average Curve (absolute) calculates the average curve of for example *n* DSC signals in unit [mW/mg] in the following way:

$$\langle DSC[\tfrac{mW}{mg}]\rangle_{abs} = \frac{\sum_{i=1}^{n}\left(DSC[\frac{mW}{mg}]\right)_i \cdot m_{0i}}{\sum_{i=1}^{n} m_{0i}} = \frac{\sum_{i=1}^{n} (DSC[mW])_i}{\sum_{i=1}^{n} m_{0i}} \quad (1)$$

In case of Average Curve (absolute), the samples with higher initial mass m_{0i} contribute more to the resulting average curve (in relative units) than samples with less initial mass. Average Curve (absolute) is recommended for inhomogeneous samples and for very small initial sample masses where the baseline correction has a significant impact.

Average Curve (relative) calculates the average of for example *n* DSC signals in unit [mW/mg] in the following way:

$$\langle DSC[\tfrac{mW}{mg}]\rangle_{rel} = \frac{\sum_{i=1}^{n}\left(DSC[\frac{mW}{mg}]\right)_i}{n} \quad (2)$$

In case of Average Curve (relative), each individual curve equally contributes to the average curve (in relative units).

In the limit that all initial sample masses m_{0i} are identical, formulas (1) and (2) for Average Curve (absolute) and Average Curve (relative) are exactly the same.

SuperPosition of, for example, *n* DSC signals in unit [mW/mg] is calculated according to the equation

$$\langle DSC[\tfrac{mW}{mg}]\rangle_{sup} = \sum_{i=1}^{n}\left(DSC[\tfrac{mW}{mg}]\right)_i \cdot r_i \quad (3)$$

where r_i to be defined by the user are the mass ratios (percentages) of each curve to the superposition with $r_i = 0 \ldots 100\%$ and $\sum_{i=1}^{n} r_i = 100\%$.

The purpose of *SuperPosition* is the creation of a synthetic curve simulating a measurement on a mixture of the individual samples. This implies that the individual samples did not react with each other so that a true measurement on the mixture was really like the superposition of the individual curves. On the other hand: Differences between the curve of the true measurement of a physical mixture and the *SuperPosition* result is a sign for an interaction between the mixture components (e.g., between the active pharmaceutical ingredient and the excipient in a pharmaceutical formulation).

The formulas (1), (2) and (3) above being valid for DSC can easily by adapted to thermogravimetry (TGA) where we consider mass changes Δm in units [%] and [mg]:

$$\langle \Delta m\ [\%]\rangle_{abs} = \frac{\sum_{i=1}^{n}(\Delta m\ [\%])_i \cdot m_{0i}}{\sum_{i=1}^{n} m_{0i}} = \frac{\sum_{i=1}^{n}(\Delta m\ [mg])_i}{\sum_{i=1}^{n} m_{0i}} \quad (4)$$

$$\langle \Delta m\ [\%]\rangle_{rel} = \frac{\sum_{i=1}^{n}(\Delta m\ [\%])_i}{n} \quad (5)$$

$$\langle \Delta m\ [\%]\rangle_{sup} = \sum_{i=1}^{n}(\Delta m\ [\%])_i \cdot r_i \quad (6)$$

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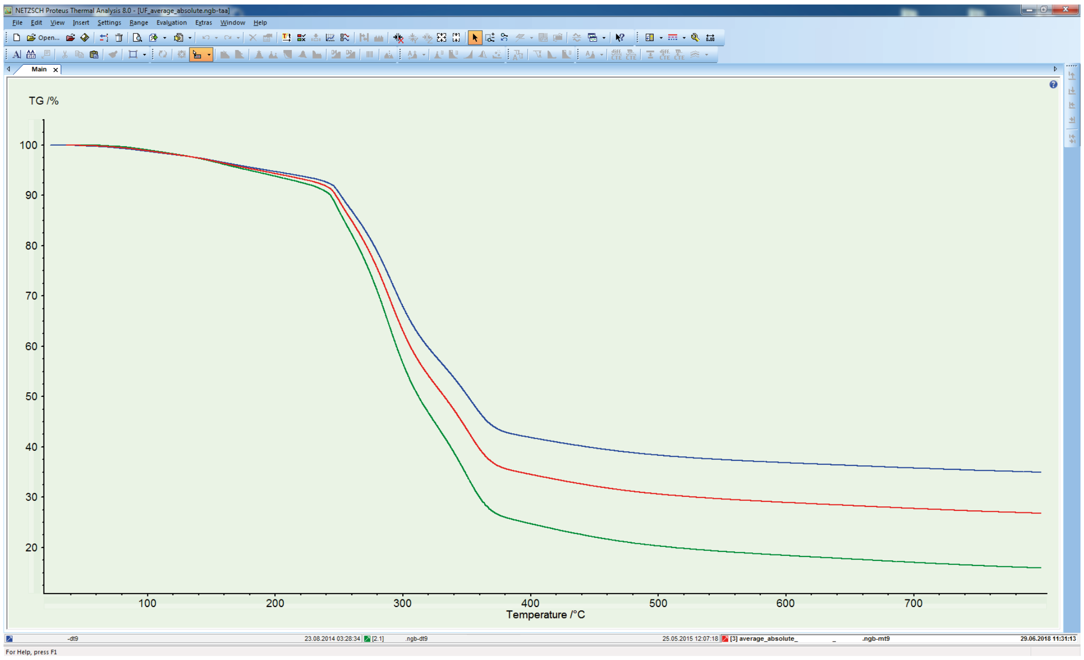
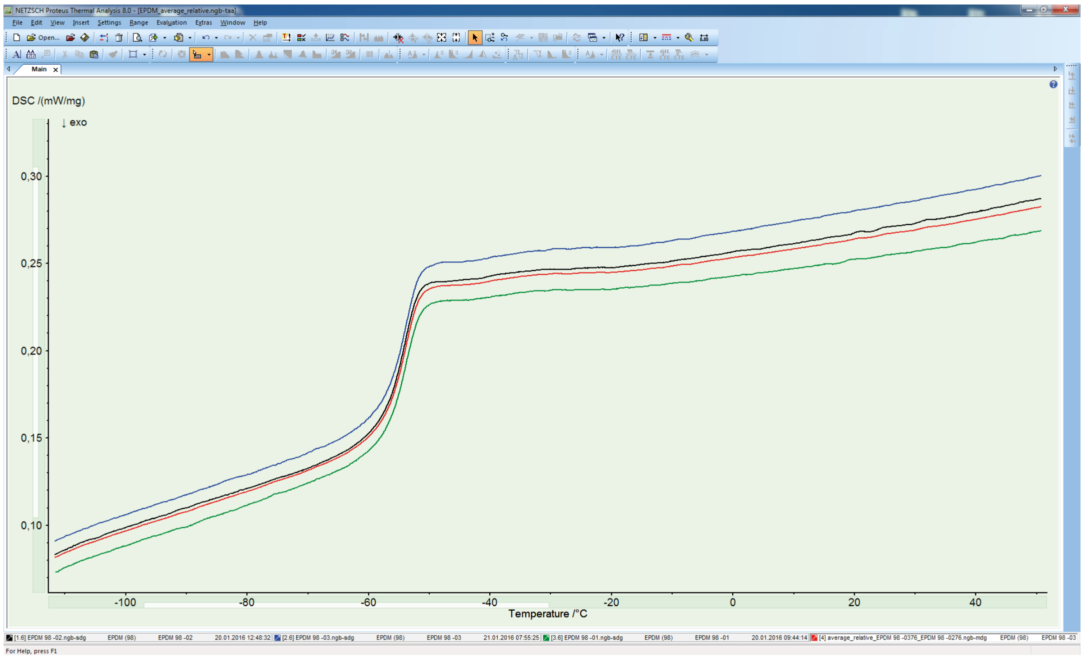
Figure 2 shows an example for using the Average Curve (absolute) function: Thermogravimetric analysis was done on two samples of the same composite material. Due to the inhomogeneity of the sample material, the resulting TGA curves are significantly different. The average curve (absolute) is not exactly in the middle of the two measured curves, but slightly closer to the curve with the higher initial mass, as explained above.

Depicted in figure 3 are three DSC measurements on EPDM (2nd heating curves) along with the Average curve (relative). This example demonstrates that averaging leads to a better signal-to-noise ratio.



2 Two TGA measurements and the average curve (absolute) of an inhomogeneous composite material. One sample had an initial mass of 13.73 mg (blue curve) and the second sample an initial mass of 10.29 mg (green curve); the average curve (absolute) is displayed in red.



3 Three DSC measurements (blue, black and green) on EPDM with initial sample masses of about 10.3 mg (2nd heating curves). Furthermore displayed in red is the average curve (relative).

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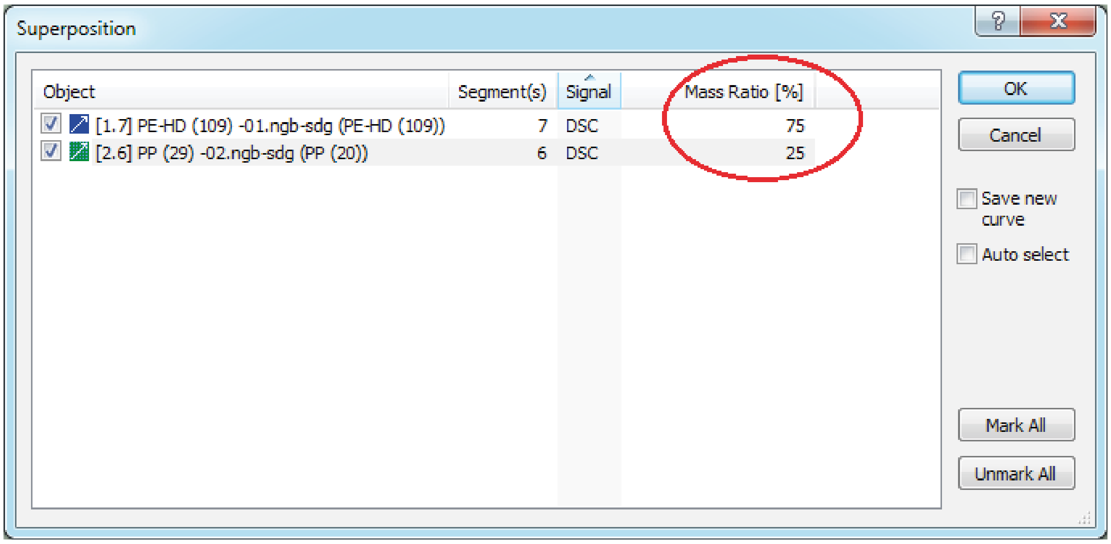
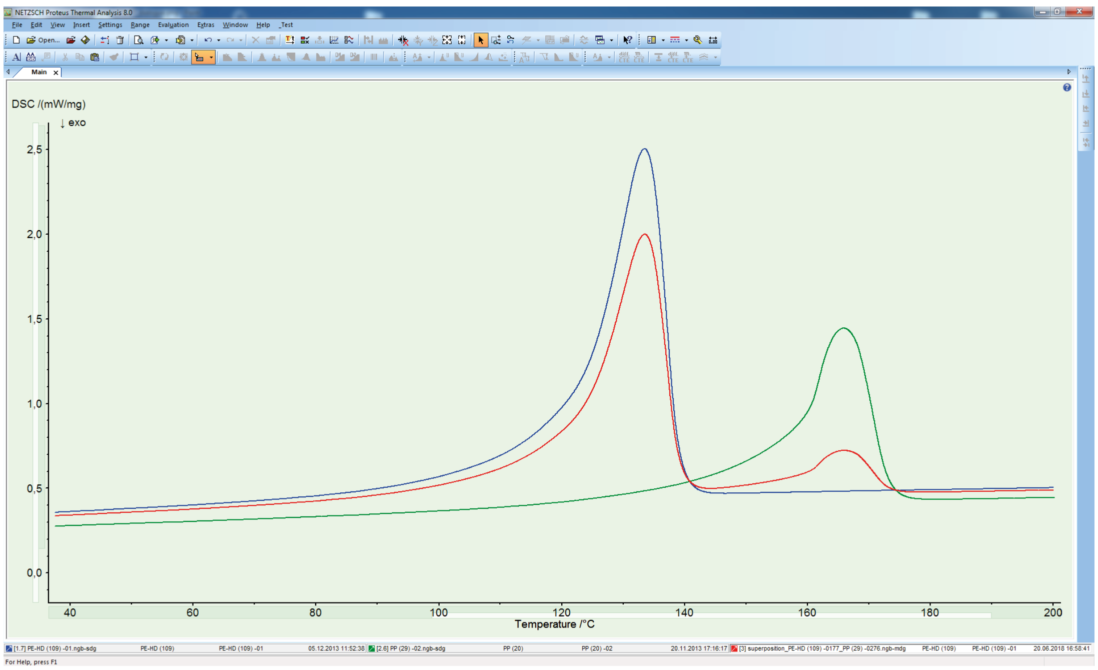
An exemplary application of the *SuperPosition* function is displayed in figures 4a and 4b where two DSC measurements on two different polymers, pure PE-HD and pure PP, were used for calculation of a superposition (75% PE-HD + 25% PP). In general, the number of individual curves is, of course, not limited to two.



4a Software dialog for *SuperPosition*. In this example, the user typed in 75% as the desired mass ratio of PE-HD manually, the software automatically adapted the PP content to 25% (highlighted in red).



4b DSC curves for pure PE-HD (blue), pure PP (green) and the calculated superposition (75% PE-HD + 25% PP, red).

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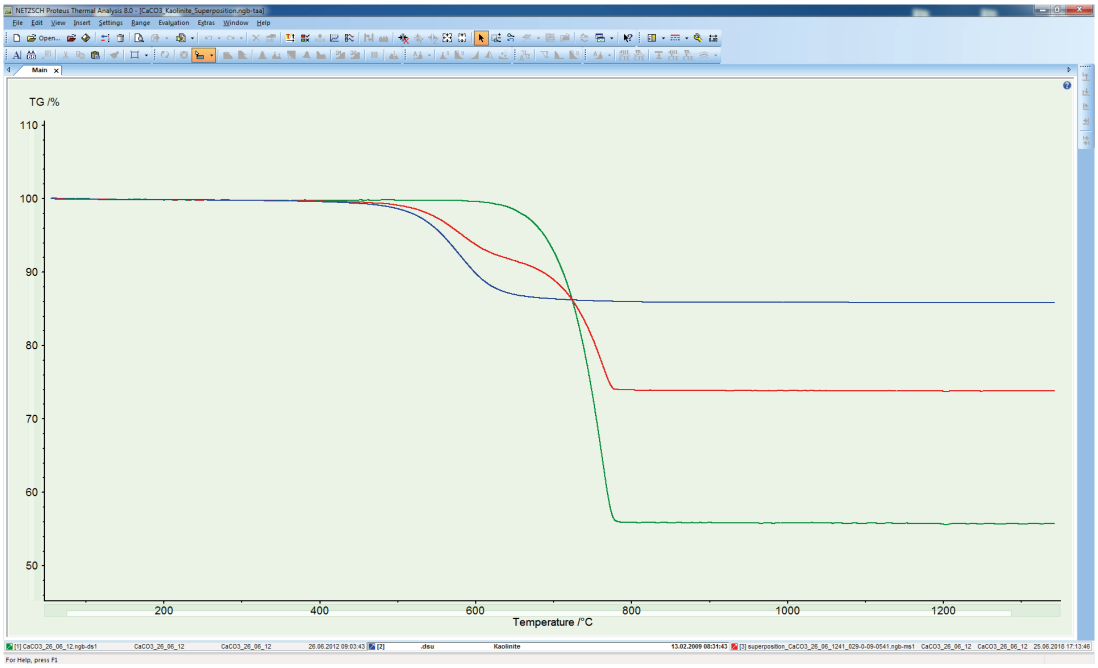
Figure 5 depicts an application of the *SuperPosition* function on two TGA curves (60% kaolinite + 40% $CaCO_3$).

Finally, it must be emphasized that calculated curves from the Average and *SuperPosition* functions can both be

- evaluated using the *Proteus®* analysis functions, even with *AutoEvaluation*.
- used for *Identify*, for example, added to a user's library. This allows for easy comparison of, e.g., a true measurement on a mixture with the calculated curve from *SuperPosition* and with measurements on the pure substances via *Identify* (similarity and overlay of curves).



5 TGA curves for kaolinite (blue), pure $CaCO_3$ (green) and the calculated superposition (60% kaolinite + 40% $CaCO_3$, red).

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