The New *SuperRes*® Mode 'Dynamic Scan'

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The *SuperRes*® option, available for TGA and STA instruments, has so far included the 'Start/Stop', 'Step-Iso' and 'Dynamic' modes, in which the heating rate is automatically controlled during the measurement in such a way that, in the event of mass losses, a user-defined constant rate of mass change is maintained. For better clarity, the names of these modes have been therefore extended with „RCM" (Rate Controlled Mass Change), starting with Proteus® version 9.10.

As of *Proteus*® version 9.10, the additional *SuperRes*® mode 'Dynamic Scan' is available. In this mode, the heating rate is reduced whenever the sample undergoes mass changes, resulting in improved resolution of the mass-change steps compared to a constant heating rate. In this mode, however, the system does not control to a constant rate of mass change which, in turn, simplifies the measurement definition. A further advantage is that at a high maximum heating rate, the total measurement time is usually relatively short. Overall, the new 'Dynamic Scan' mode thus enables fast overview measurements while still providing good resolution of the mass-change steps.

Activation and Settings

Figure 1 shows how to activate *SuperRes*® in the settings of a measurement or method definition. It is also advisable to activate *TG-BeFlat*® because with *SuperRes*®, no correction measurement is possible due to the adaptive temperature control.

Measurement Definition ?

Setup | Header | Temperature Program | Calibrations | Last Items

Property	Value	Action	Help
Instrument name	TG309 Libra Classic (TG30900A-0011) on USBc24-414/6	Modify instrument name	?
Furnace	TG309 Ceramic Std TC: S (0 ... 1060 °C/ 30 K/min)		
Sample carrier	TG Alumina Sh P 9mm TC: P (-200 ... 1200 °C)		
Measurement mode	TG		
Crucible (¹)	• PtRh20 85 µl, open (... 1700 °C)	Crucibles Viewer...	?
Start criteria	5,0 K, Delay: 00:30 mm:ss Stability criteria enabled unconditionally: HR: 0,100 K/min, TG signal stability rate: 0,0500 mg/min Heat.: (30 K/min,20 min), Cool.: (50 K/min,30 min)	Modify start criteria	?
Devices	MFCs(4), Valve Box		?
Valve box (¹)	Off		?
FTIR coupling (¹)	Off		
QuadStar trigger support (¹)	Off		?
TG BeFlat support (¹)	On	Modify similarities	?
Temperature modulation (¹)	Off		?
SuperRes (¹)	On		?
TG-Stability detection (¹)	Off		?
Weighing mode (¹)	Manual input		?
Emergency temperature	Enhancement to maximum segment temperature: 10 K	Redefine enhancement	?

Current hardware temperature range is from 0 °C to 1060 °C

(¹) Item has multiple possible values.

1 Activation of *SuperRes*® in the settings of a measurement or method definition.

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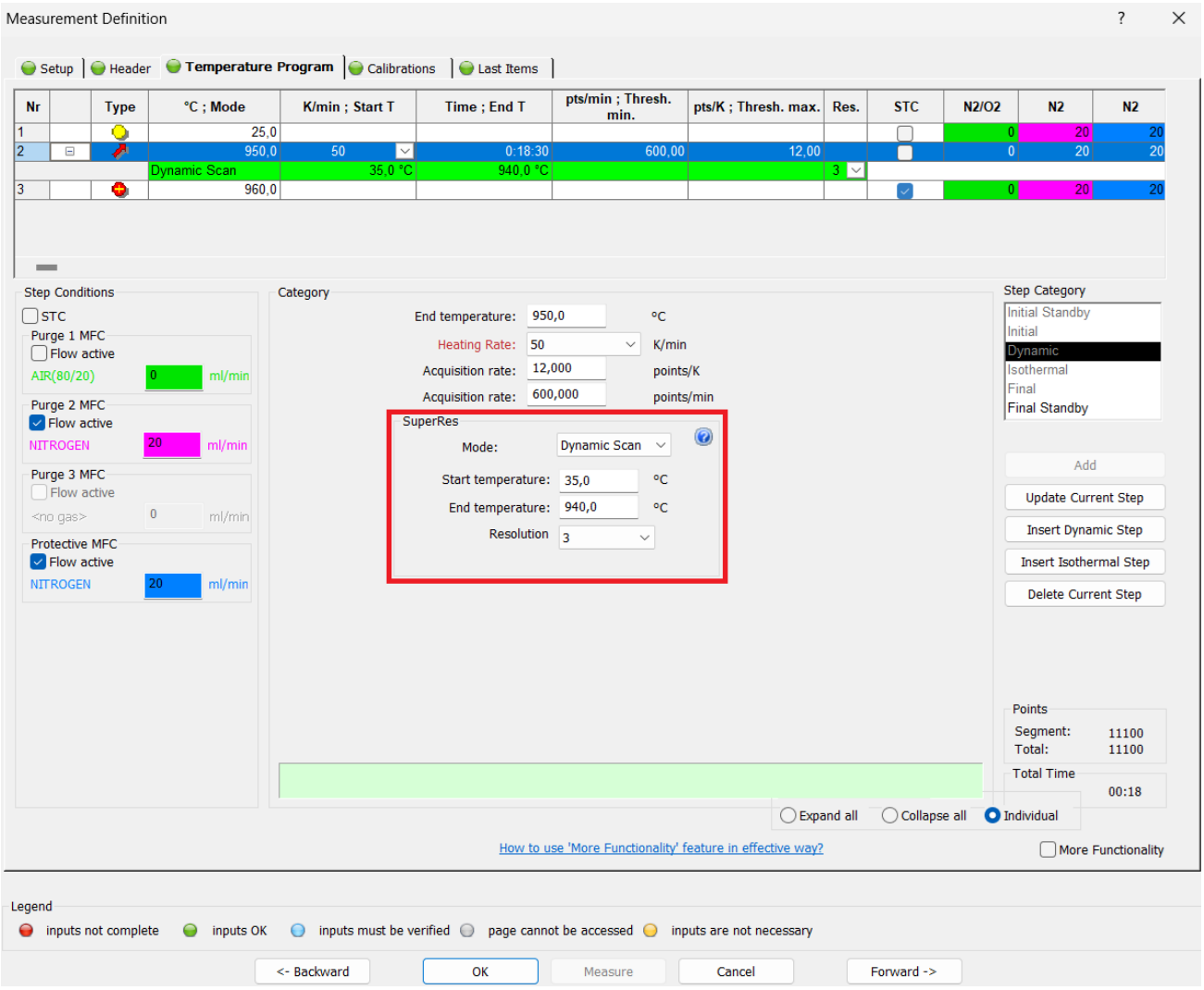
In Figure 2, the area outlined in red shows which settings of *SuperRes*® are available within the temperature program of a measurement or method definition. The user has selected the 'Dynamic Scan' mode. The values for the start and end temperatures of the *SuperRes*® temperature control are set to 10 K higher/lower by default than the initial/final temperatures of the dynamic temperature segment. In the example shown, the maximum heating rate is 50 K/min; in the *SuperRes*® 'Dynamic Scan' mode, the user can select values 10, 20, 50 or 100 K/min. The 'Resolution' parameter (abbreviated as 'Res.'), which is preset to a value of 3, can be set by the user between 1 and 5. The higher this value, the more strongly the heating rate is reduced during the measurement as a function of the detected rate of mass change.



2 Settings of *SuperRes*® (mode: 'Dynamic Scan') within the temperature program of a measurement or method definition.

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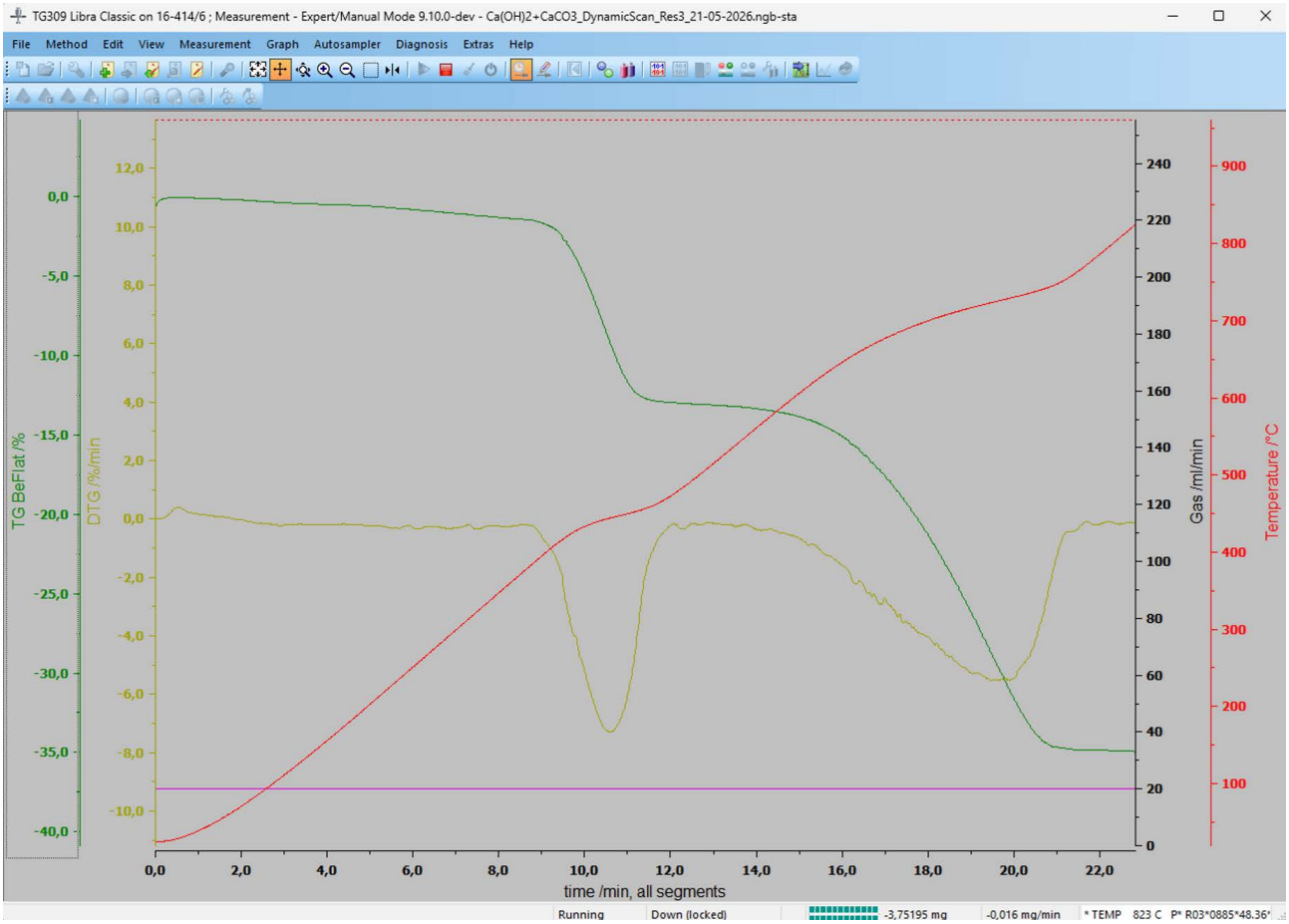
Figure 3 illustrates the effect of *SuperRes*® during a running measurement; the corresponding measurement definition is shown in Figure 2. It can be seen how the temperature rise is slowed as the absolute value of the rate of mass change increases. Further details are discussed below.



3 Mass changes (green curve), rate of mass change (olive curve) and temperature (red curve) as a function of time during a running measurement with *SuperRes*® (mode: 'Dynamic Scan').

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Application Examples

Figures 4 show the results of three TGA measurements, each performed on a 50:50 mixture of $Ca(OH)_2$ and $CaCO_3$ using a TG 309 *Libra*® *Classic*. The measurements were carried out on samples with approximately 10 mg sample mass using an open PtRh crucible in a dynamic N_2 atmosphere (40 ml/min). In one measurement, a constant heating rate of 20 K/min was applied while in the other two measurements, *SuperRes*® in 'Dynamic Scan' mode was used. The maximum heating rate was 50 K/min in each case, but different resolution parameters (Res. 3 and Res. 5) were selected. In principle, the mass-loss step between approximately 400°C and 450°C is due to the release of water from $Ca(OH)_2$, while the mass-loss step in the approximate temperature range between 600°C and 750°C can be attributed to the decomposition of $CaCO_3$, in which CO_2 is released. The small mass loss below approximately 350°C is most likely due to adsorbed moisture and impurities. Figure 4a shows that especially in the *SuperRes*® measurement with Res. 5, the mass-loss steps are significantly sharper, i.e., they occur within narrower temperature intervals — compared to the measurement at a constant heating rate, which is also reflected in the curve of the rate of mass change DTG in units of %/K.

In this context, the time course of the measurements shown in Figure 4b is decisive: as expected for the two *SuperRes*® measurements, the temperature rise was slowed during the mass-loss steps, i.e., the heating rate was automatically reduced there, as already shown for the measurement with Res. 3 in Figure 3. In regions where no significant mass losses occurred, the heating rate was at its maximum of 50 K/min, so here, heating was faster than in the measurement at a constant heating rate of 20 K/min. As a result, the *SuperRes*® measurement with Res. 3 took in total only about half as long as the measurement at a constant heating rate of 20 K/min. This means that *SuperRes*® delivered a substantial time saving in this measurement while still providing good temperature resolution of the mass-loss steps (see Figure 4a). The total duration of the *SuperRes*® measurement with the highest resolution Res. 5 was approximately equal to the total duration of the measurement at a constant heating rate of 20 K/min. However, the mass-loss steps in this *SuperRes*® measurement were considerably sharper.

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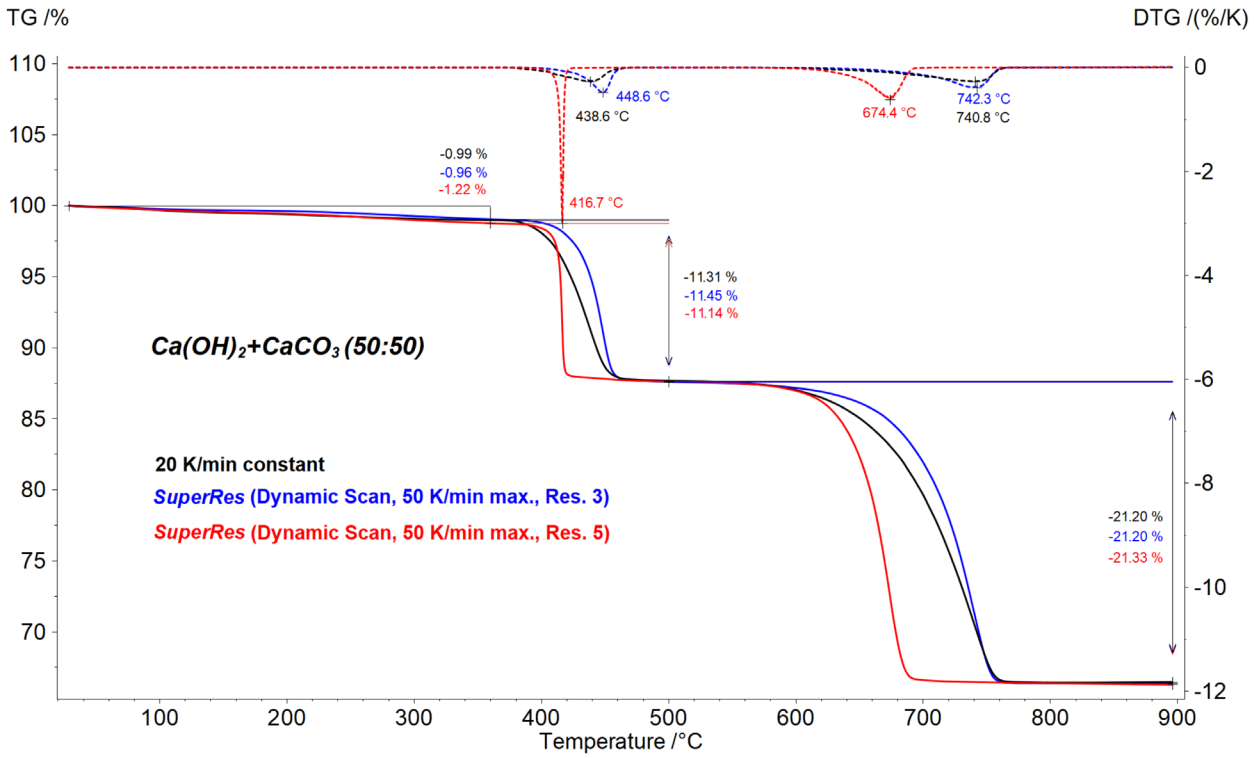
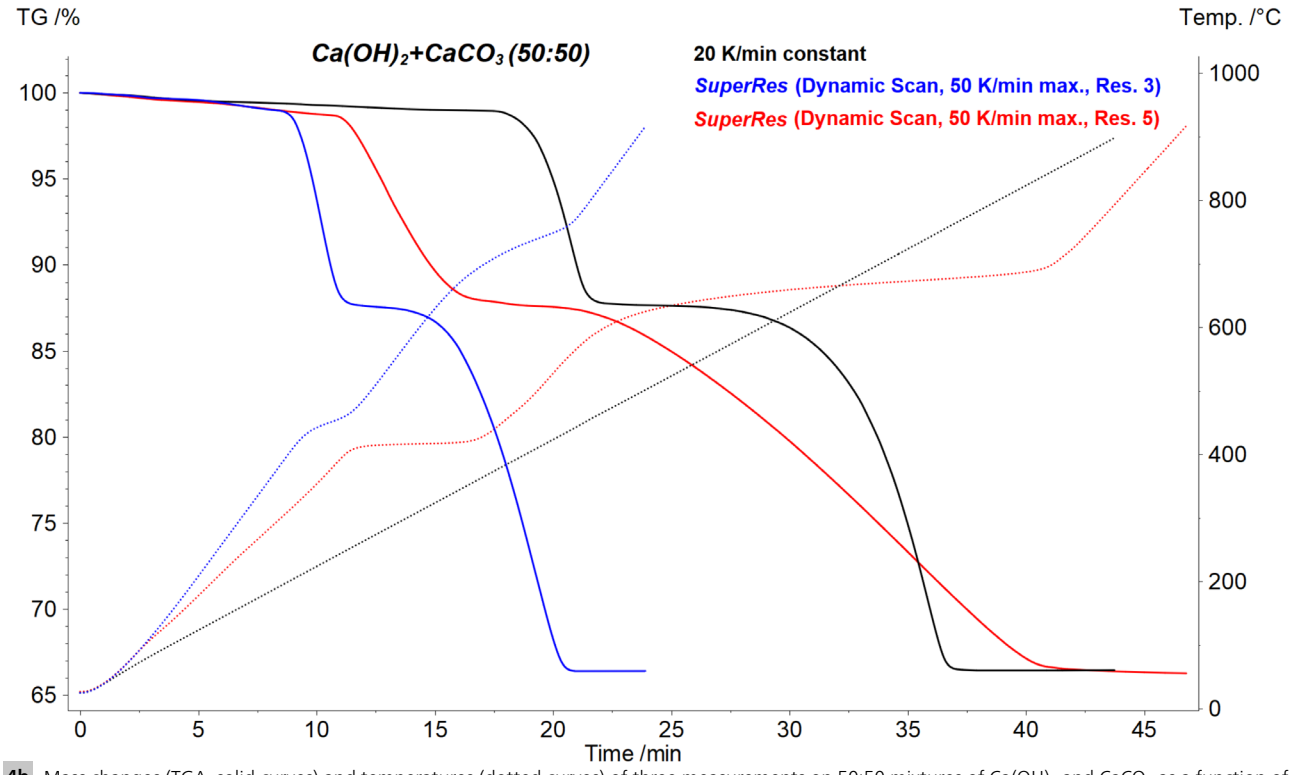


4a Mass changes (TGA, solid curves) and rates of mass change (DTG, dashed curves) of three measurements on 50:50 mixtures of $Ca(OH)_2$ and $CaCO_3$ as a function of temperature. One measurement was carried out at a constant heating rate of 20 K/min (black curves), the other two measurements each with *SuperRes*® (blue and red curves).



4b Mass changes (TGA, solid curves) and temperatures (dotted curves) of three measurements on 50:50 mixtures of $Ca(OH)_2$ and $CaCO_3$ as a function of time. These are the same measurements as shown in Fig. 4a.

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A further application example is shown in Figures 5. All three TGA measurements were each performed on a sample composed in 50:50 proportions of NR (natural rubber) and SBR (styrene-butadiene rubber); this was not a true rubber blend, but rather pieces of NR and SBR, each with a mass of approximately 5 mg, were weighed together into an open Al_2O_3 crucible. The TG 309 *Libra*® *Classic* was used again, and the measurements were performed in a dynamic N_2 atmosphere (40 ml/min) like before. One measurement was performed at a constant heatig rate of 50 K/min, one at a constant heating rate of 10 K/min, and one with *SuperRes*® in 'Dynamic Scan' mode (maximum heating rate of 50 K/min, Res. 3). Measurements on the individual NR and SBR materials had also been carried out before. It is therefore known that both NR and SBR show mass loss below approximately 350°C under the measurement conditions used, but that the main decomposition of NR takes place in the temperature range of 350°C to 400°C, whereas SBR decomposes mainly in the range of 400°C to 500°C. It is evident from Figure 5a that the two main decomposition steps of NR and SBR strongly overlap when measured at a constant heating rate of 50 K/min and also at 10 K/min. The mass-loss steps are shifted to higher temperatures at higher heating rates. In the measurement with *SuperRes*®, the two main mass-loss steps were considerably better separated, which is also visible in the sharper DTG peaks.

Figure 5b shows that the total duration of the *SuperRes*® measurement was about 12 minutes longer than the measurement at a constant heating rate of 50 K/min, but about 34 minutes shorter than the measurement at a constant heating rate of 10 K/min — even though the separation of the main mass-loss steps was considerably better (see Figure 5a).

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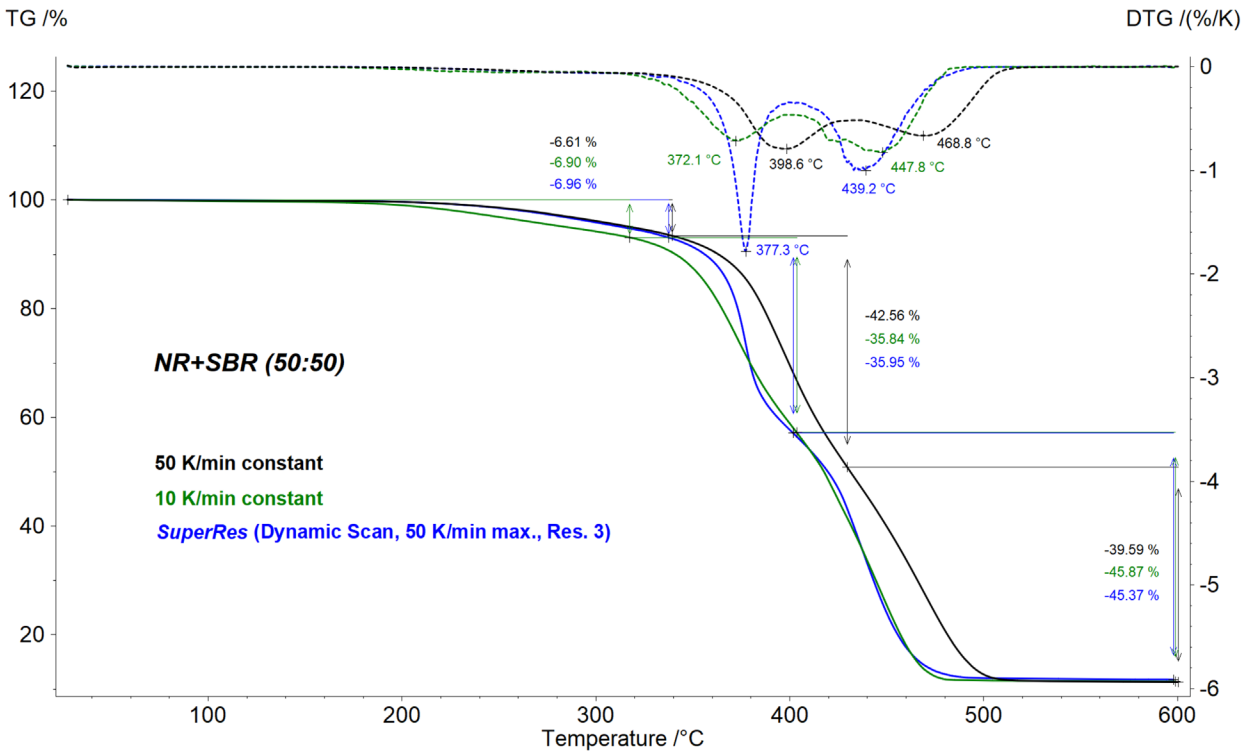
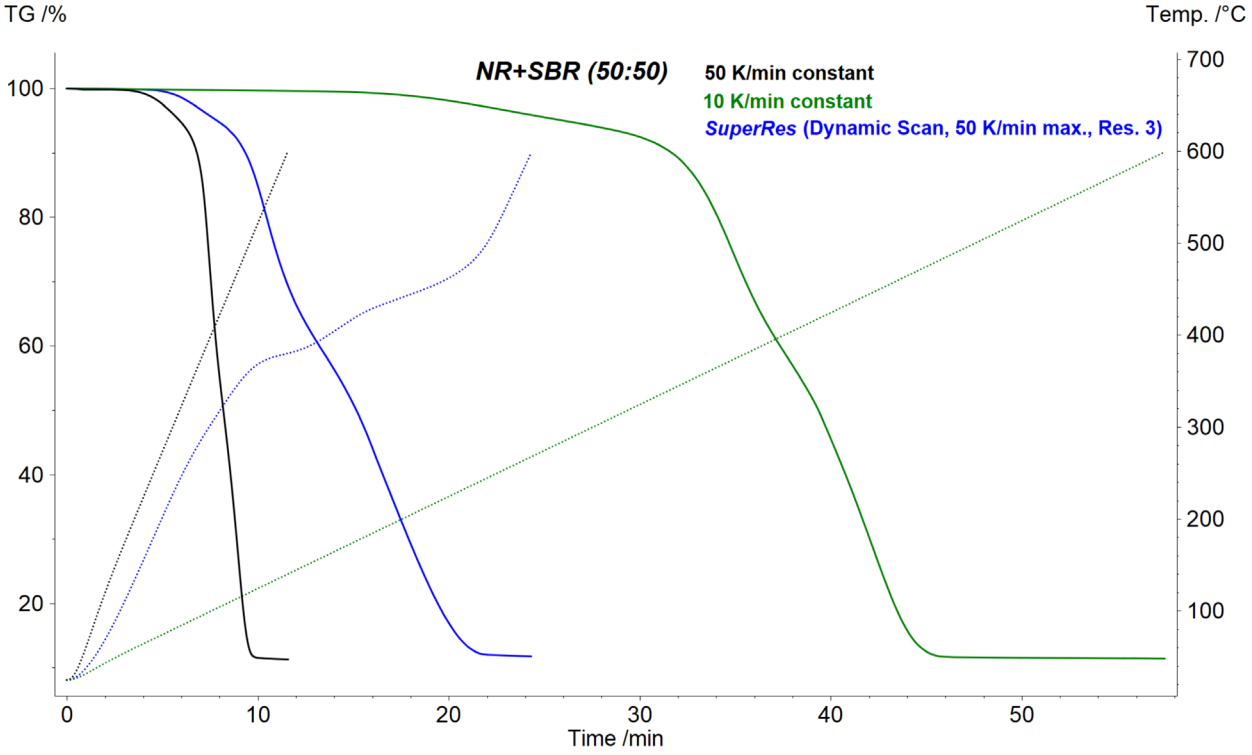


5a Mass changes (TGA, solid curves) and rates of mass change (DTG, dashed curves) of three measurements on 50:50 mixtures of NR and SBR as a function of temperature. Two measurements were carried out at constant heating rates of 50 and 10 K/min respectively (black curves); the third measurement was performed with *SuperRes*® (blue curve).



5b Mass changes (TGA, solid curves) and temperatures (dotted curves) of three measurements on 50:50 mixtures of NR and SBR as a function of time. These are the same measurements as shown in Fig. 5a.

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Summary

Starting with *Proteus*® version 9.10, the additional *SuperRes*® mode 'Dynamic Scan' is available for TGA and STA measurements. In this mode, the heating rate of the measurement is automatically reduced as a function of the rate of mass change, resulting in improved resolution of the mass-loss steps. By means of a single measurement parameter, the user can easily and intuitively influence the extent of the heating-rate reduction, and thus the resolution. It was shown that the *SuperRes*® 'Dynamic Scan' mode, when using a high maximum heating rate, enables fast and efficient overview measurements with good resolution of the mass-change steps.

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