

THERMAL APPLICATIONS NOTE

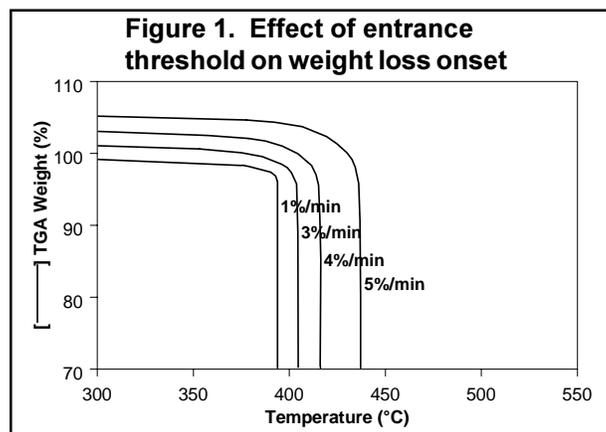
Optimizing Stepwise Isothermal Experiments in Hi-Res™ TGA

The ability to separate closely occurring events is important in most analytical techniques because incomplete separation can adversely affect the accuracy and reproducibility of the results. For example, in thermogravimetric analysis (TGA), resolution directly affects the quantitation and identification (by evolved gas analysis) of successive degradations (weight losses). In TGA, the experimental variables affecting resolution are sample size, heating rate, and purge gas composition. Of those, varying heating rate has the most dramatic effect on resolution.

TA Instruments supplies four different variable heating rate algorithms (approaches), which can be used either alone or in combination, as part of its High Resolution TGA (Hi-Res) option [PN 952251-901]. Those approaches include dynamic rate, constant reaction rate, constant heating rate, and stepwise isothermal. (See publication TA023 for a more detailed description of those approaches.)

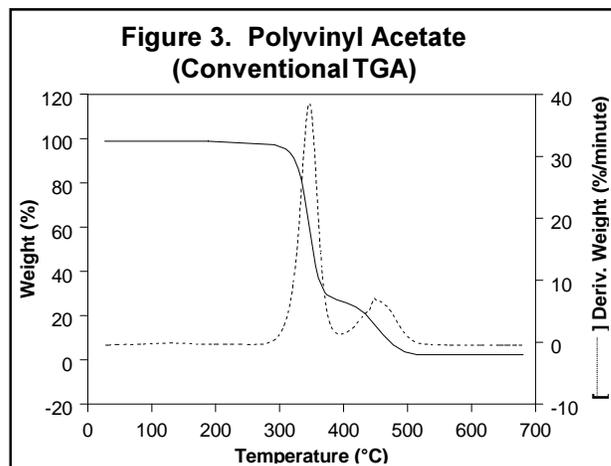
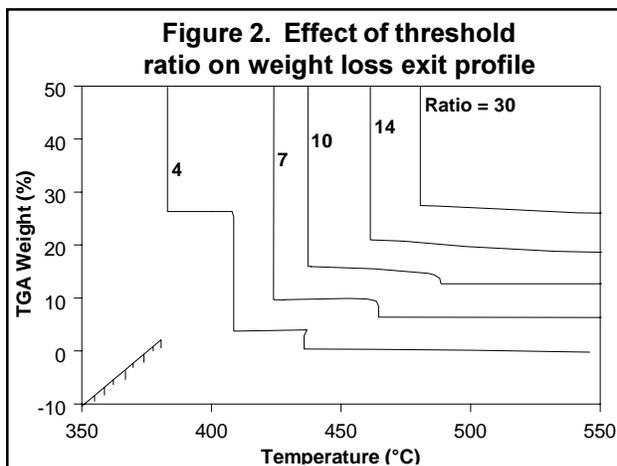
Stepwise isothermal is the most difficult to use of the four approaches because improper choice of conditions can lead to experimental artifacts (typically extra weight loss peaks). The following procedure is designed to avoid those artifacts and optimize results.

1. Select a relatively fast underlying heating rate - typically 20°C/minute. Using a faster underlying heating rate yields the best compromise between experimental time and resolution.
2. Conduct a scouting run at this constant underlying heating rate (without thresholds), plotting the TGA weight loss derivative curve in units of % per minute.
3. Choose an entrance threshold for the subsequent stepwise isothermal experiments based on 1/10 - 1/15th of the derivative peak height. Figure 1 illustrates the effect of entrance threshold on the decomposition onset of a single-stage decomposition.



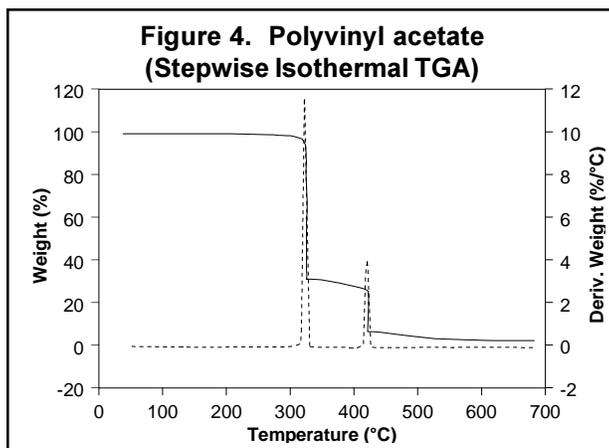
[Note: the curves shown are offset to avoid overlap.] As the entrance threshold is decreased, the transition becomes sharper (a desirable effect) but the experiment becomes longer (e.g., 145 minutes at a 1 %/minute threshold versus 45 minutes at a 5 %/minute threshold). For this reason, larger values are selected for the entrance threshold. Another effect of decreasing the entrance threshold is that the transition moves, as expected, to a lower temperature.

4. Choose an exit threshold for the subsequent stepwise isothermal experiments based on 1/15th of the entrance threshold or less. Figure 2 illustrates the effects of varying the entrance/exit threshold ratio. A common exit threshold of 0.1 %/min. is used in the comparison shown here. [Note: the curves are offset in the z axis for display purposes.] These results clearly show that a larger entrance/exit threshold ratio is required, because if the two thresholds are too close in size, additional “apparent” weight losses occur. These weight losses are not real but are merely the result of the underlying heating rate being resumed before a specific weight loss is complete. In this case, using an entrance/exit threshold ratio of 30 provided the best results.



5. Conduct the stepwise isothermal experiment using the conditions chosen in steps 1-4.

Figures 3 and 4 show the resolution improvement obtained for a typical material (polyvinylacetate) using appropriate stepwise isothermal parameters. Figure 3 shows the results using conventional constant heating rate TGA at 20°C/minute. Two weight losses are observed at about 350 and 450°C. The first weight loss peak height in the derivative is roughly 40 %/minute. 1/15th of that height (3%/minute) is chosen as the entrance threshold. From this, an exit threshold of 0.2%/minute (1/15th of the entrance threshold) is chosen. Using the same process for the second weight loss, entrance and exit thresholds of 1%/minute and 0.05%/minute respectively are chosen. Figure 4 shows the stepwise isothermal results under those conditions. The weight losses obtained are crisp and easy to quantify. Furthermore, the return to baseline in the derivative curve between the two weight losses indicates the desired resolution has been achieved.



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