

## HIGH RESOLUTION THERMOGRAVIMETRIC ANALYSIS - A NEW TECHNIQUE FOR OBTAINING SUPERIOR ANALYTICAL RESULTS

### INTRODUCTION

Resolution, the ability to separate closely occurring events, is an important criterion for most analytical instrument techniques since it effects the ability to obtain accurate, quantitative results. Thermal Analysis techniques are no exception to this basic rule. A good example is thermogravimetric analysis (TGA) which measures weight changes with temperature, providing information about material compositional analysis and thermal stability. Resolution of successive TGA weight losses is important for obtaining accurate, reproducible weight change values, as well as accurate component identification in the evolved decomposition gases by FTIR (Fourier transform infrared) or mass spectroscopy.

In thermal analysis, the variables affecting resolution for a specific hardware design are typically sample size, heating/cooling rate, and purge gas composition. Generally, smaller sample sizes, slower heating/cooling rates, and higher thermal conductivity purge gases (e.g., helium) result in improved resolution. Varying (slowing) heating rate has proven to be a particularly effective method for enhancing resolution in TGA experiments. The literature contains several references (1,2,3) which clearly illustrate that adjusting (slowing) the heating rate during weight changes improves resolution. J. Rouquerol in 1964 (1) used vacuum TGA and based heating rate control on sensing pressure increases associated with the evolved decomposition gases. Paulik & Paulik (2) adjusted TGA heating rate as necessary to achieve a constant rate of reaction (weight change). Sorenson (3) in 1978 used stepwise isothermal control to enhance TGA resolution. All three of these approaches resulted in better resolution, but with substantial increases in experimental time.

TA Instruments has recently introduced another approach which delivers superior TGA resolution without the time trade-off present in the earlier literature approaches. In fact, this approach (patent pending\*) often provides better results in less time than conventional constant heating rate TGA. This new approach is included as part of a high resolution TGA (Hi-Res™ TGA) accessory for the TA Instruments TGA 2950 Thermogravimetric Analyzer which enables the operator to choose among several different heating rate

approaches to obtain the best compromise of resolution and productivity for a specific situation.

### PRINCIPLES OF OPERATION

Although the TA Instruments Hi-Res™ TGA accessory involves software algorithms which control the TGA furnace, it is the unique design of the TGA 2950 Thermogravimetric Analyzer which makes the ultimate resolution enhancements possible. Figure 1 shows the furnace schematic for the TGA 2950. The TGA 2950 is a vertical balance system which features 1.5gm capacity, 0.1µg sensitivity, and an ambient to 1000°C temperature range. It contains three features critical to Hi-Res™ TGA:

### TGA 2950 SCHEMATIC - SAMPLE AREA

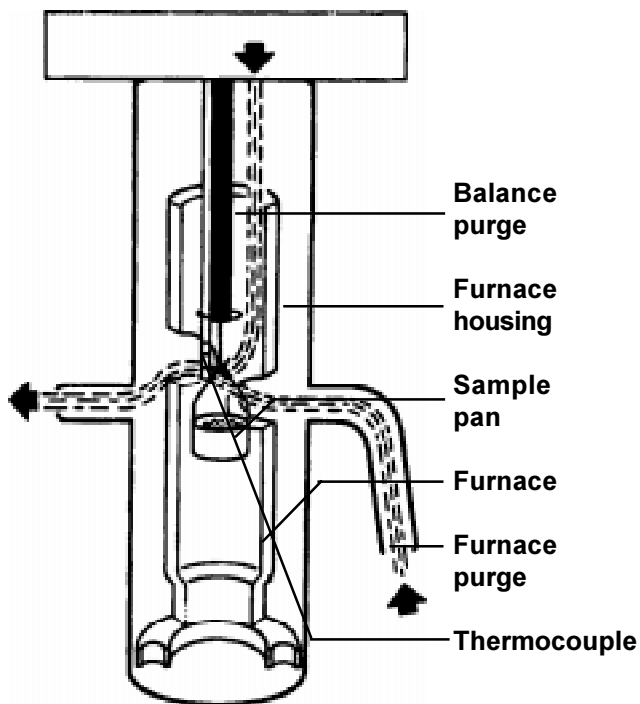


Figure 1

- Single thermocouple design. The TGA 2950 uses a single thermocouple located close to the sample for controlling the furnace and for monitoring sample temperature. This arrangement facilitates the rapid temperature servo response necessary to Hi-Res™. The relatively low furnace mass also contributes to this rapid response.

- Horizontal purge gas flow. The open design of the TGA 2950 sample pans combined with a horizontal purge gas flow ensures good interaction between the sample and purge gas, as well as rapid removal of decomposition products so that undesired recombination effects do not broaden the weight loss peaks. For high resolution experiments, the use of an inert purge gas such as nitrogen, helium or argon is recommended. Oxygen or air as the purge gas effects the decomposition thermodynamics such that overlap between closely occurring decompositions is increased. Using a gas such as helium has the additional benefit of being an ideal carrier gas for evolved gas analysis.

- High balance sensitivity. Since the heating rate control is linked to weight change, the ability to sense small weight changes is important to achieve optimum control.

#### HI-RES™ TGA ALGORITHMS

The TA Instruments Hi-Res™ TGA accessory consists of four different variable heating rate algorithms (approaches) which can be used either alone or in combination to obtain the optimum results on a specific material. The basis for each of the algorithms is described below:

- Dynamic Rate. This is the TA Instruments patent-pending approach. It differs from the other approaches in that the heating rate of the sample material is dynamically and continuously varied in response to changes in the sample's rate of decomposition so as to maximize weight change resolution. This approach allows very high heating rates to be used in regions where no weight changes are occurring while avoiding transition temperature overshoot.

Because the dynamic rate approach reduces heating rate smoothly and only when necessary, it is the fastest and most reliable of the various techniques. This mode gives good results with most temperature separable transitions. It is preferred for fast survey scans of unknown materials over wide temperature ranges. If no other criteria exists to select a Hi-Res™ technique, then dynamic rate is the preferred choice.

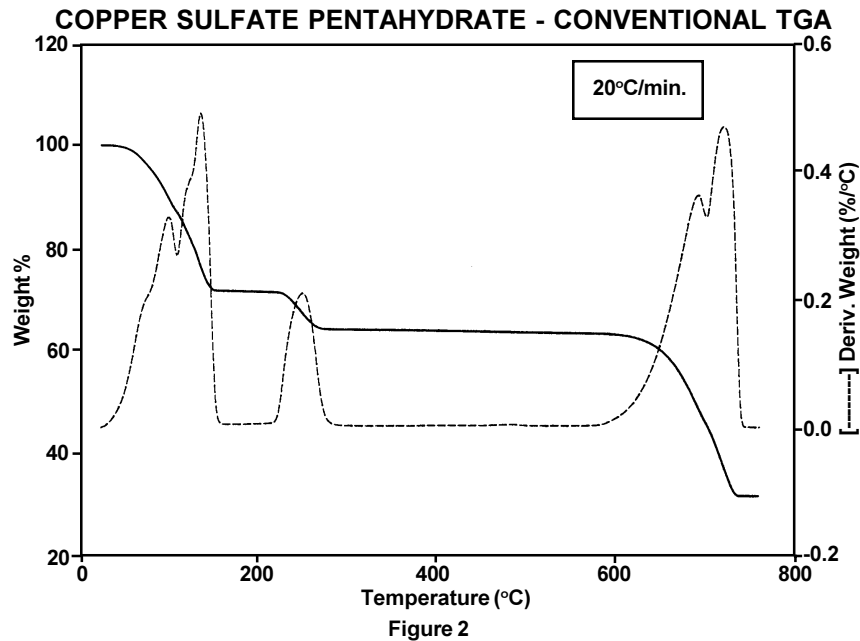
- Constant Reaction Rate. In the constant reaction rate approach the heater control system varies the temperature of the furnace as required to maintain a constant preselected rate of weight change (%/minute). Whenever the rate of weight change exceeds the percent/minute threshold, the heating rate of the furnace is reduced, even to the point of cooling if necessary. When percent/minute falls below the threshold the heating rate is increased up to the maximum specified for the ramp segment. Transition resolution is improved because sample heating is reduced or reversed during transitions allowing them to complete at the selected reaction rate before moving on to the next transition.

Constant reaction rate mode is preferred for any sample where it is important to limit or control the rate of reaction. These may include pyrotechnics, self-heating reactions, auto-catalyzing reactions and gas diffusion reactions. Constant reaction rate mode is also a good choice when it is important to accurately determine the transition temperature at a given reaction rate.

Another area where constant reaction rate heating can be helpful is when the sample material exhibits a relatively large and somewhat constant background weight change onto which is superimposed a relatively small transition. If the decomposition rate threshold is chosen to be close to the background rate at the maximum heating rate, then the heating rate will only be changed significantly when the smaller transition occurs.

- Stepwise Isothermal. The stepwise isothermal approach consists of heating at a constant rate until a weight change begins as determined by an operator chosen rate or amount of weight loss and then holding isothermally until the weight change is complete. This sequence of heating and isothermal holding is repeated for each weight change encountered.

This approach has a significant advantage over the other techniques in that the reaction onset and completion can be very carefully controlled. If the reaction rates for the decomposition are known, then the controller can be programmed to stop heating as soon as the first indication of a reaction occurs, and to continue heating once the reaction has subsided in an insignificant level. This is particularly helpful for transitions which are very closely spaced in temperature. One disadvantage of stepwise heating is the need to run several TGA scans to properly "tune" the reaction rate thresholds used to start and stop heating. Another drawback is the relatively slow heating rates required to prevent transition overshoot.

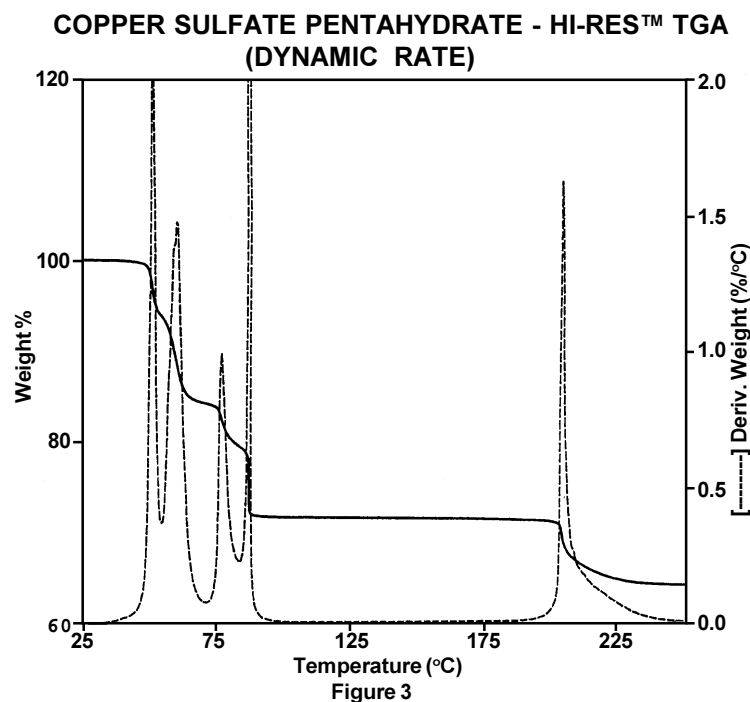


• Constant Heating Rate (Conventional TGA). In this TGA approach a constant heating rate is used throughout the experiment. Using slower heating rates, 1-2°C/minute or less, is often required to obtain any resolution enhancement from this approach.

**APPLICATIONS**

A series of applications which illustrate the power of Hi-Res™ TGA is included in this section. The example applications shown are not meant to be all inclusive, but are chosen to illustrate the type of results possible.

INORGANICS. Inorganics are convenient materials for assessing TGA resolution because they are readily available and often degrade with well-defined stoichiometric weight losses. Cupric sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) is a typical example. Figure 2 shows the conventional TGA results for cupric sulfate at 20°C/minute. The solid line indicates a series of weight losses beginning at about 70°C. These weight losses between 70°C and 250°C represent the loss of waters of hydration. Although conventional TGA provides a well-defined weight loss of the last hydration water, the initial water weight losses are difficult to resolve even using the derivative curve (broken line).



**CEMENT - HI-RES™ TGA  
(CONSTANT REACTION RATE)**

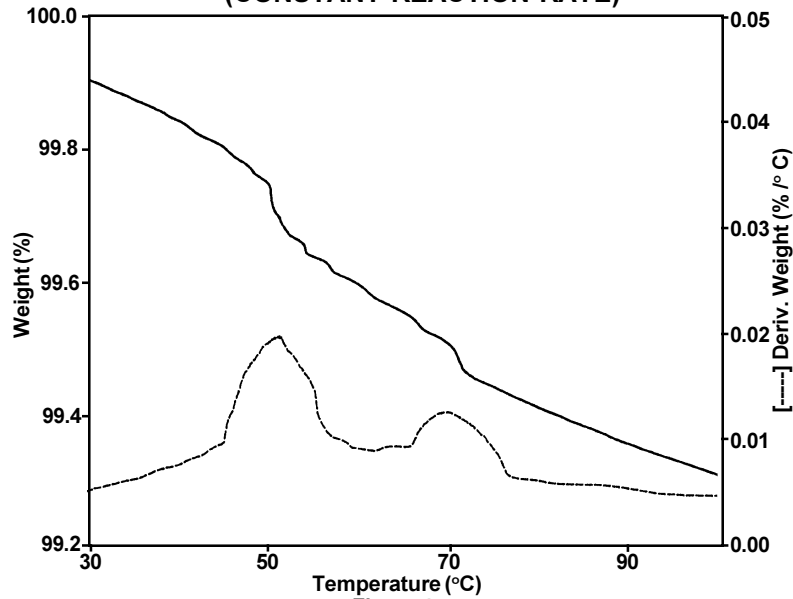


Figure 4

The Hi-Res™ TGA results (Figure 3), however, shows sharp well-resolved peaks. Figure 4 shows the results of another Hi-Res™ TGA experiment where the area of interest is waters of hydration. In this case, however, the weight losses associated with water evolution are so small and gradual that they cannot be detected by conventional TGA. Hi-Res™ TGA, in effect, provides enhanced sensitivity.

representative of pure homopolymers which typically decompose by simple, single step processes. Hence, resolution of overlapping weight loss peaks is not an issue. However, the results illustrate that the resolution as indicated by the derivative peak sharpness (wt% per °C) is improved in Hi-Res™ TGA even over conventional TGA at 1°C/minute.

**HOMO POLYMERS.** Figure 5 illustrates the comparative derivative curves for polytetrafluoro-ethylene (PTFE) using conventional and dynamic rate Hi-Res™ TGA. PTFE is

Furthermore, the Hi-Res™ TGA results are achieved in less time than conventional TGA results at 20°C/minute. This is a perfect example of Hi-Res™ TGA's value as a survey technique.

**POLYTETRAFLUOROETHYLENE (PTFE) DECOMPOSITION  
COMPARISON OF DERIVATIVE CURVES**

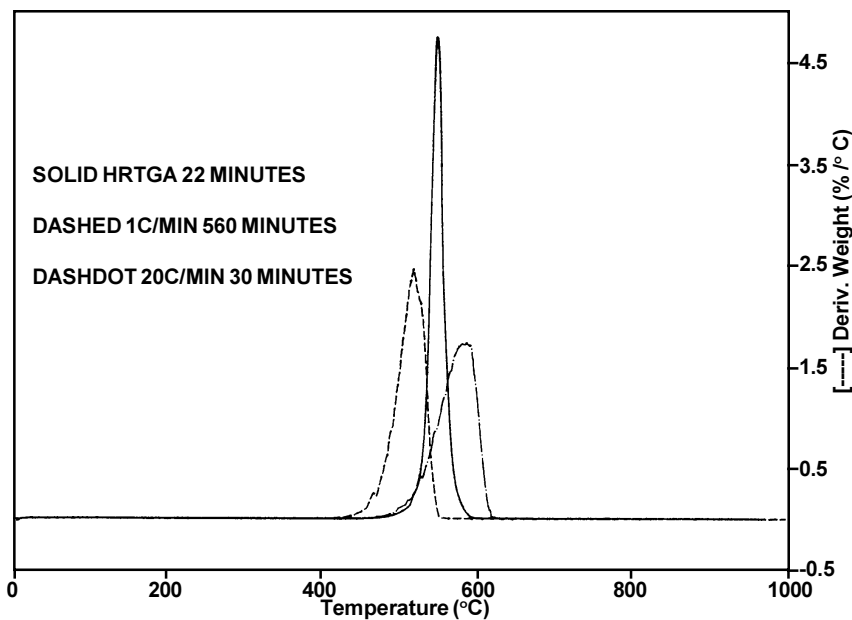


Figure 5

The shift of the decomposition to lower temperature in the Hi-Res™ TGA and 1°C/minute conventional TGA curves is as expected. In fact, these decomposition temperatures are more representative of the theoretical isothermal values.

homopolymer polymethylmethacrylate (PMMA). The polymer was prepared to be a pure homopolymer. The results, indicate, however, that a small quantity of impurity, possibly unreacted methylmonomer or even polyethylmethacrylate, is present. Conventional TGA does not resolve this impurity.

Figure 6 shows the Hi-Res™ TGA survey results for another

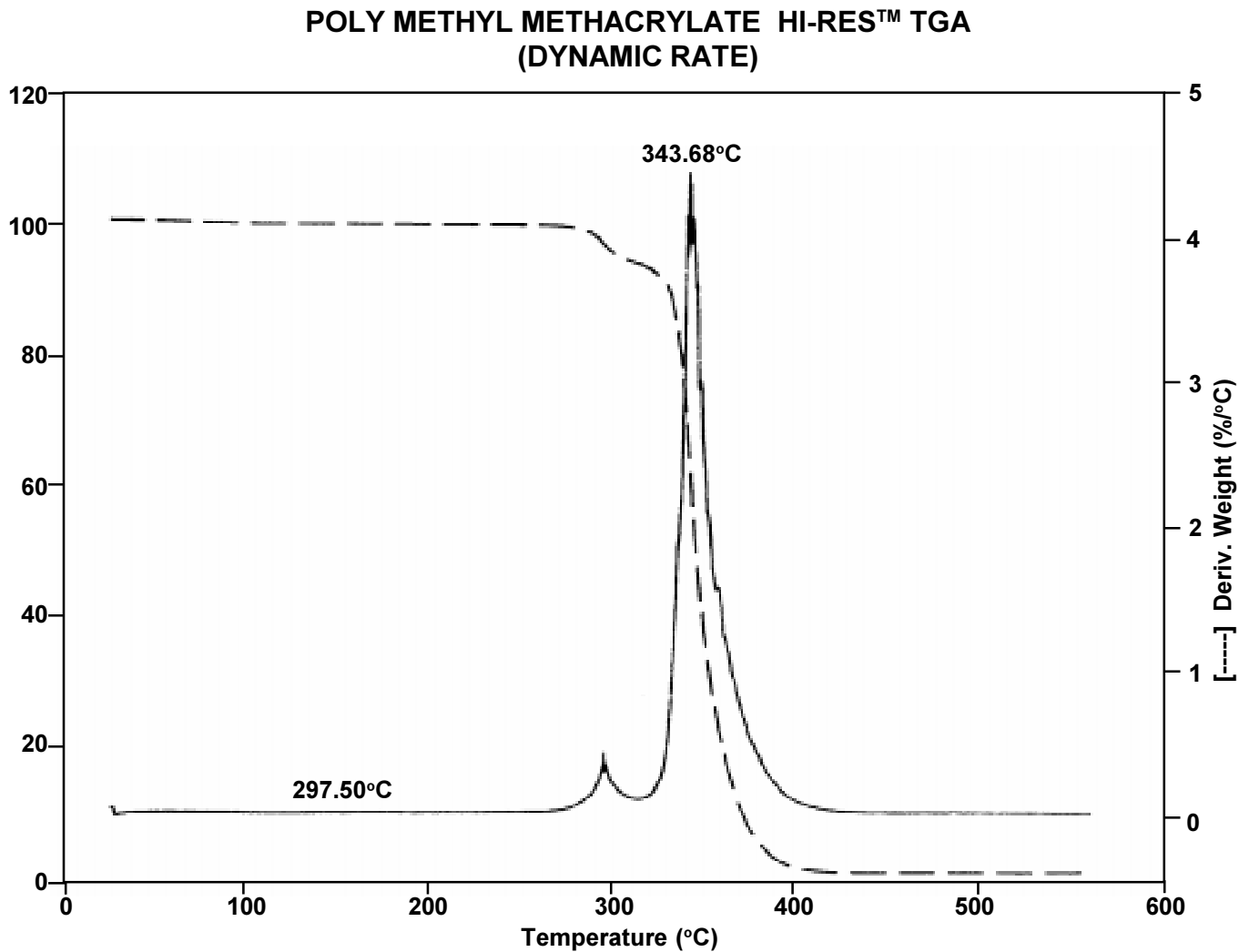


Figure 6

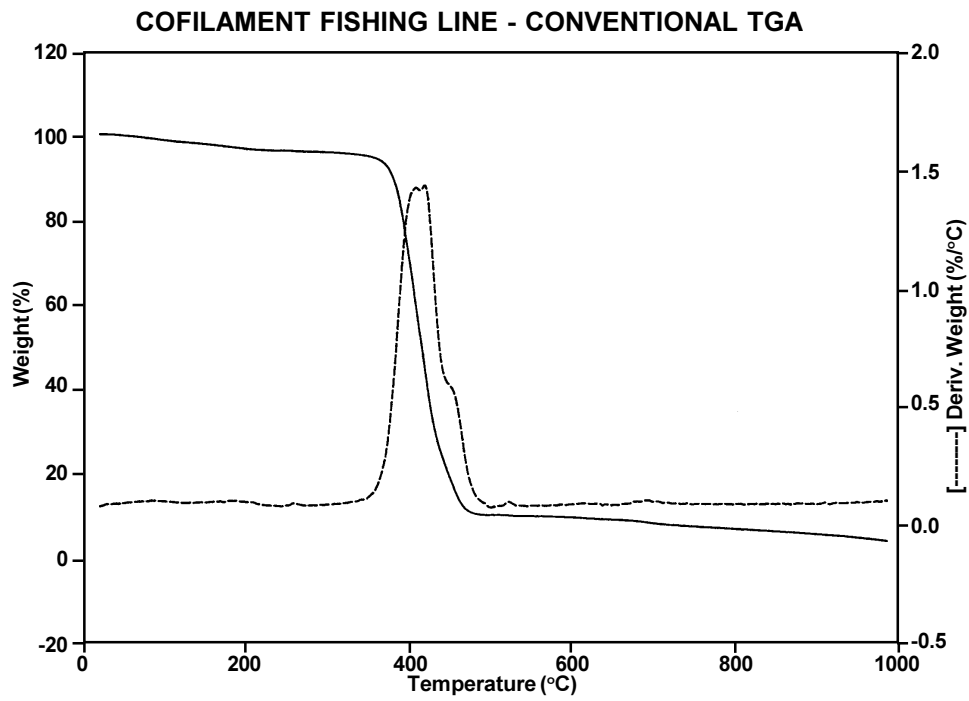


Figure 7

Hi-Res™ TGA also has value for quantifying homopolymers in finished commercial products where more than one homopolymer is present. Figures 7 and 8 show the conventional and Hi-Res™ TGA results for a cofilament fishing

line. Both runs took about 20 minutes, but the Hi-Res™ TGA results provide a much better resolution of the individual homopolymer weight losses.

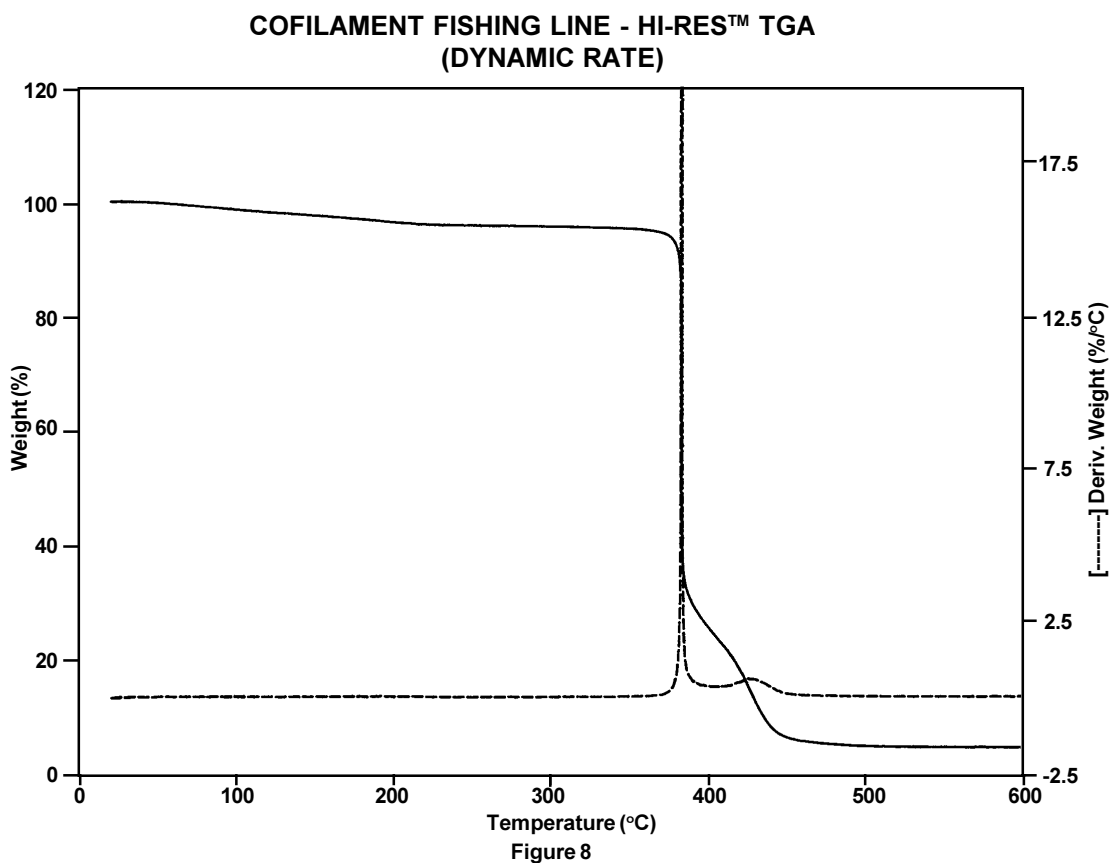
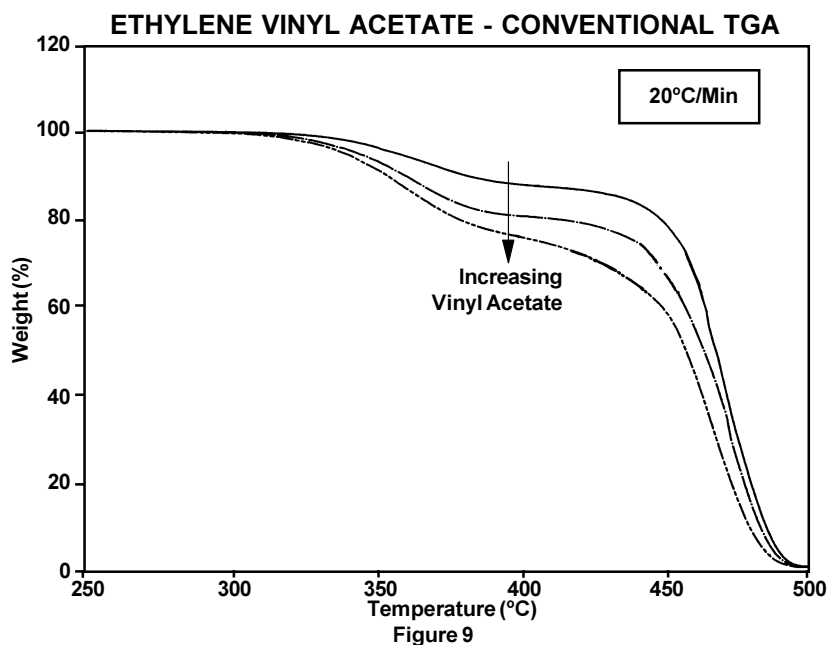


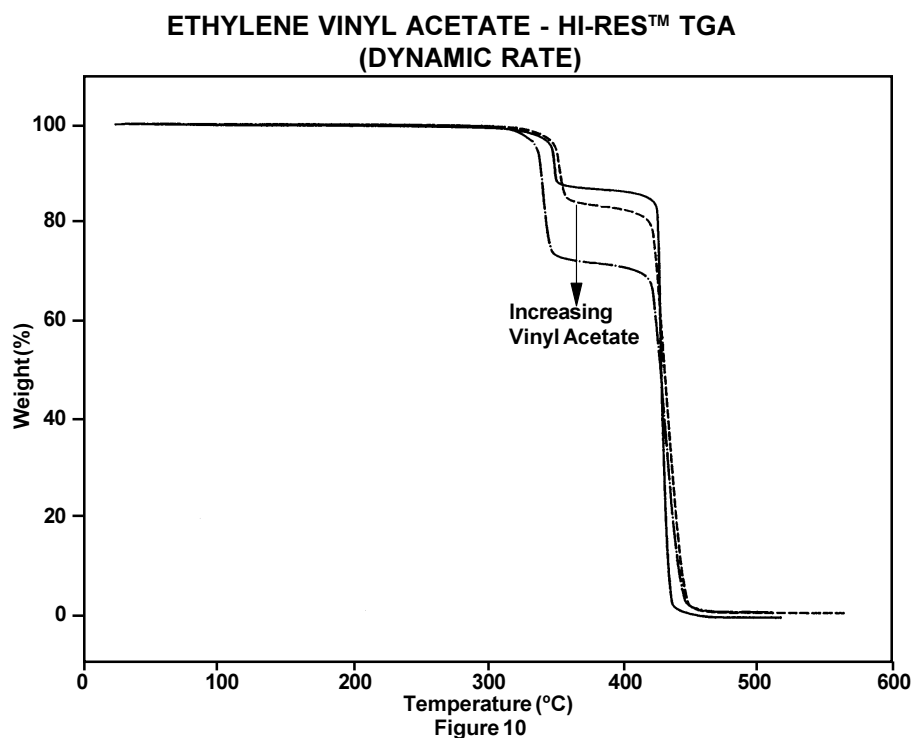
Figure 8



POLYMER BLENDS. Polymer blends represent a large class of valuable materials which are difficult to evaluate by conventional TGA and which, therefore, represent a large opportunity for Hi-Res™ TGA.

Ethylene vinyl acetate (EVA) is a common copolymer which illustrates the ability of TGA to determine the relative percentages of the polymer present based on the degradation profile. In nitrogen, EVA degrades in a two step process, where the first weight loss corresponds to acetic acid. Using

a weight ratio, which accounts for the vinyl acetate/acetic acid stoichiometry, it is possible to determine the % vinyl acetate present in the copolymer (4). Figure 9 shows the weight loss curves for several different EVA formulations by conventional TGA. Although it is clearly evident that the formulations are different, there is some opportunity for operator subjectivity when choosing the initial weight loss completion and hence, the amount of vinyl acetate present. Figure 10, on the other hand, illustrates the results of EVA materials using Hi-Res™ TGA. With Hi-Res™ TGA, it is easy to determine when the first weight loss is complete.



**EVA FORMULATION 1 - HI-RES™ TGA  
(DYNAMIC RATE)**

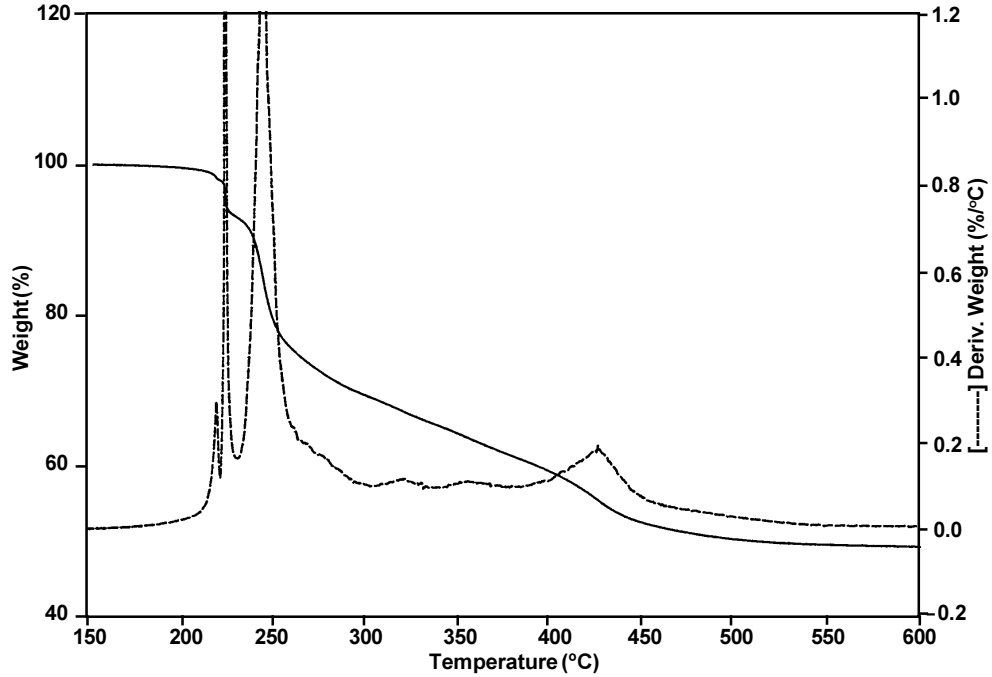


Figure 11

The presence of flame retardant or other additives, which further increase the complexity of the materials' weight loss profile, provides additional indication of the benefit of Hi-Res™ TGA. Figures 11-13 are Hi-Res™ TGA curves for EVA with different additives. These survey scans obtained in air clearly show different weight loss profiles which can

either be used quantitatively, or qualitatively as "fingerprints" to identify different formulations. The profiles for these EVA formulations in nitrogen are not as unique as in air/oxygen indicating that atmosphere also needs to be considered when attempting to optimize resolution.

**EVA FORMULATION 2 - HI-RES™ TGA  
(DYNAMIC RATE)**

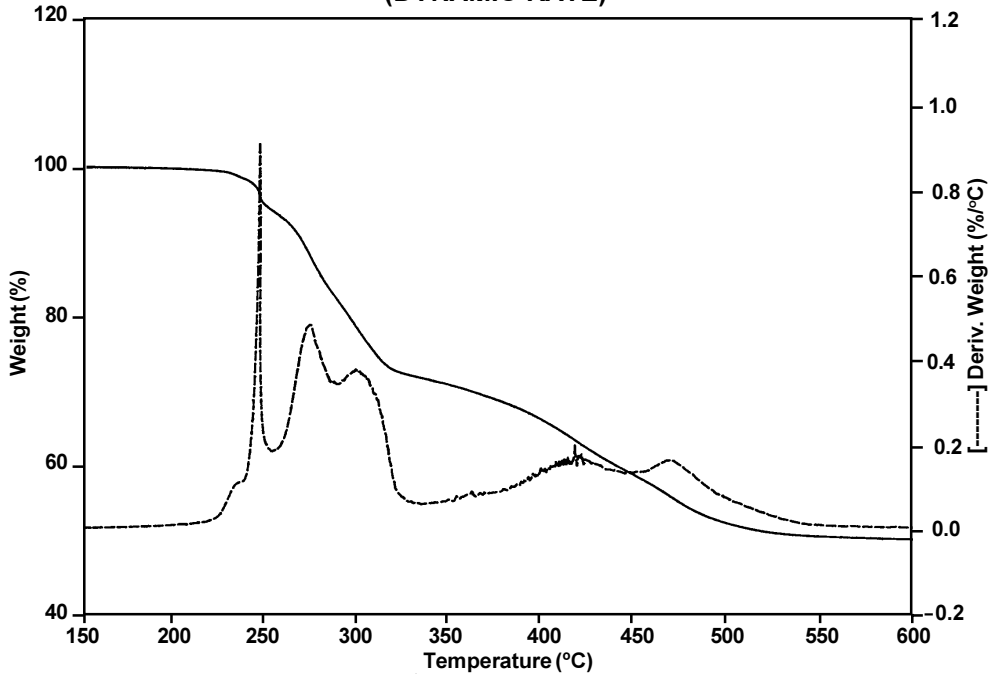


Figure 12



**EVA FORMULATION 3 - HI-RES™ TGA  
(DYNAMIC RATE)**

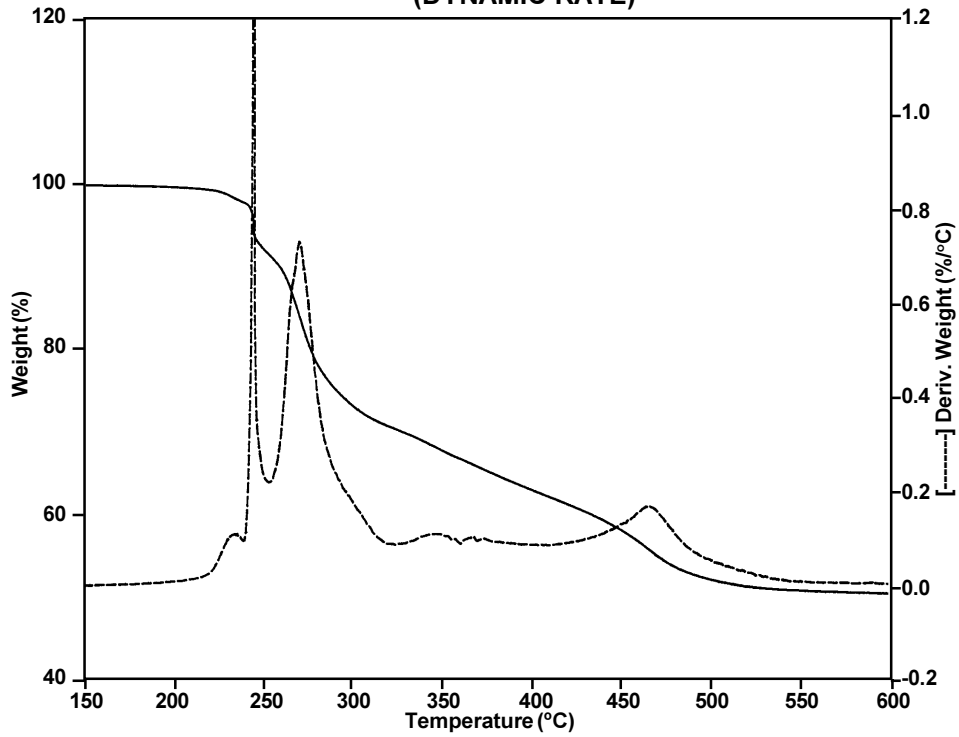


Figure 13

ABS is another common polymer blend. Figure 14 shows the comparative derivative curves for an ABS formulation evaluated by conventional (dashed line) and Hi-Res™ TGA

(solid line). The Hi-Res™ TGA results show resolution that is far superior to the conventional TGA curve.

**ABS - HI-RES™ TGA AND CONVENTIONAL TGA**

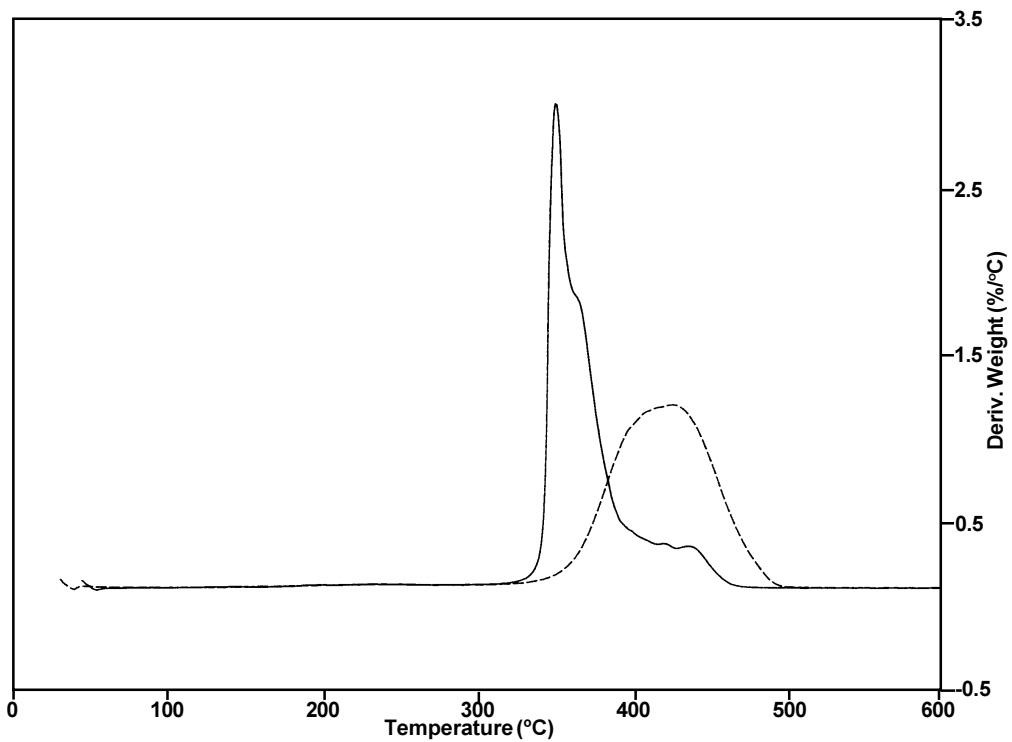
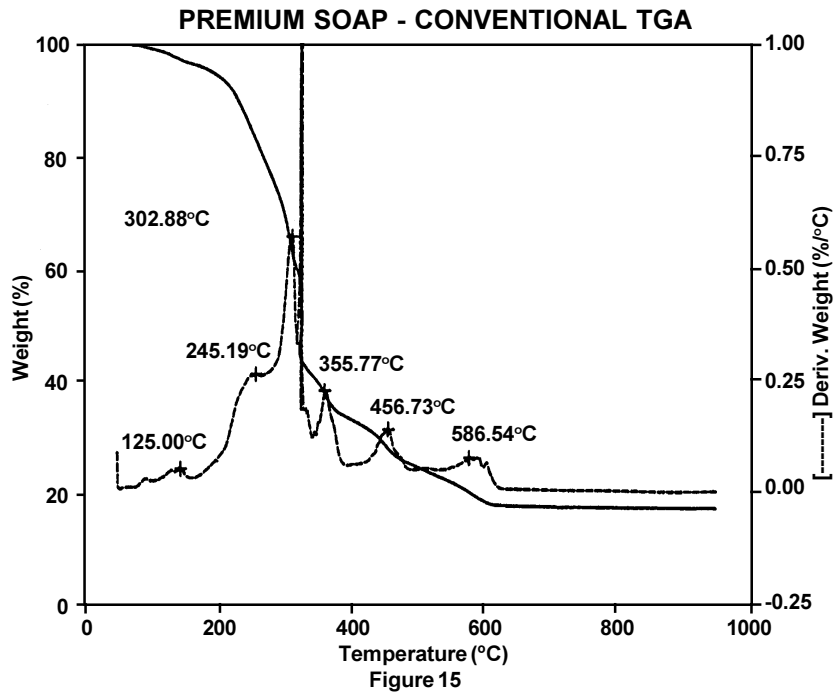
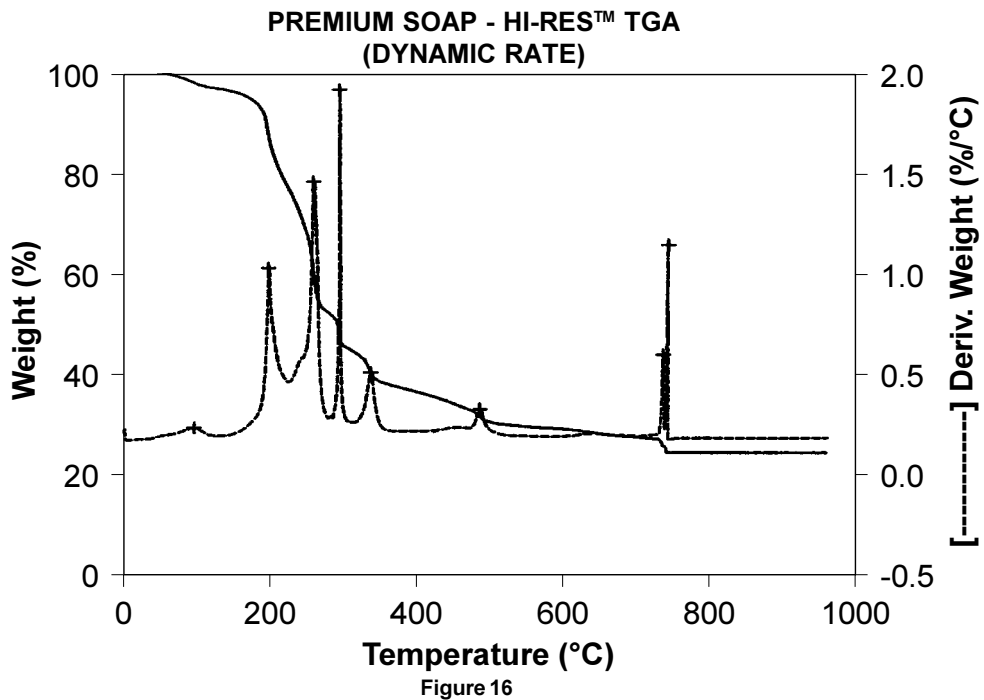


Figure 14



COMPLEX MATERIALS. Foods, natural products, and pharmaceuticals are materials that usually exhibit complex TGA profiles. Figures 15 and 16 show comparative results for a premium hand soap using conventional and Hi-Res™ TGA. The improved resolution obtained in the latter case makes it potentially easier to identify and quantify the various weight loss components. Further resolution en-

hancement of specific weight loss regions can be obtained with additional adjustment of the Hi-Res™ TGA experimental parameters. Even without further resolution improvement, however, these Hi-Res™ TGA results can be used as shown earlier with EVA to rapidly generate distinctive "fingerprints" that facilitate comparison of competitive products or checking batch-to-batch variations in formulation.



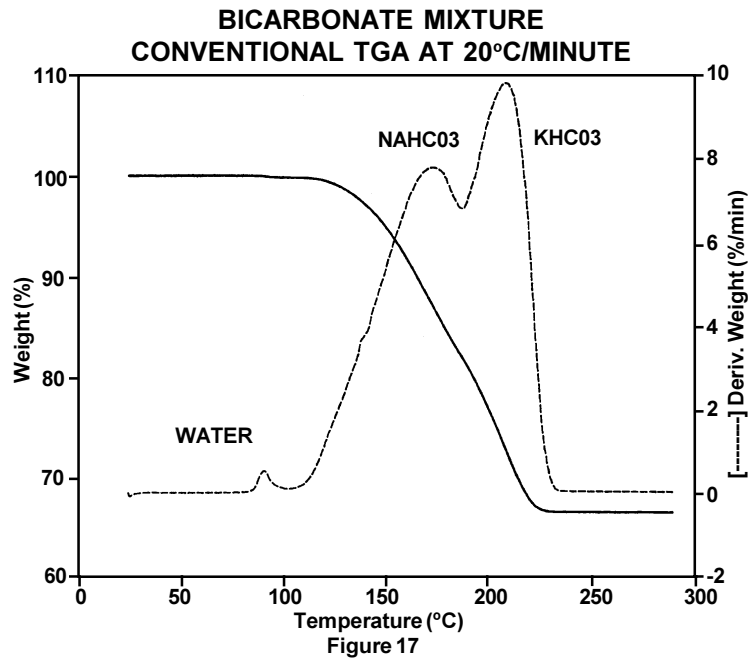


Figure 17

### CONCLUSIONS

High resolution TGA is a new technique that promises to revolutionize the quality of results that can be obtained from TGA experiments. The trade-offs that are available with Hi-Res™ TGA are illustrated in Figures 17-20. The material is a 50:50 mixture of inorganic bicarbonates which decompose less than 50°C apart. Conventional TGA at 20°C/minute shows two overlapping weight losses. Resolution improves when the conventional TGA heating rate is decreased to 1°C/minute. Using dynamic rate Hi-Res™ TGA approach yields resolution that is essentially comparable to the 1°C/minute

results, but the analysis time for the Hi-Res™ TGA approach is about 1/20th that for the conventional approach. Using the constant reaction rate Hi-Res™ TGA approach provides further resolution enhancement but with an analysis time that is closer but still less than the 1°C/minute conventional approach. (The slight temperature overshoot on the second weight loss could be eliminated by further adjustment of the algorithm parameters. However, since the result is not adversely affected, adjustment is not necessary.) As these results illustrate, the operator has the flexibility to choose the best resolution/productivity compromise for his materials. Hi-Res™ TGA is the latest in a long line of thermal analysis

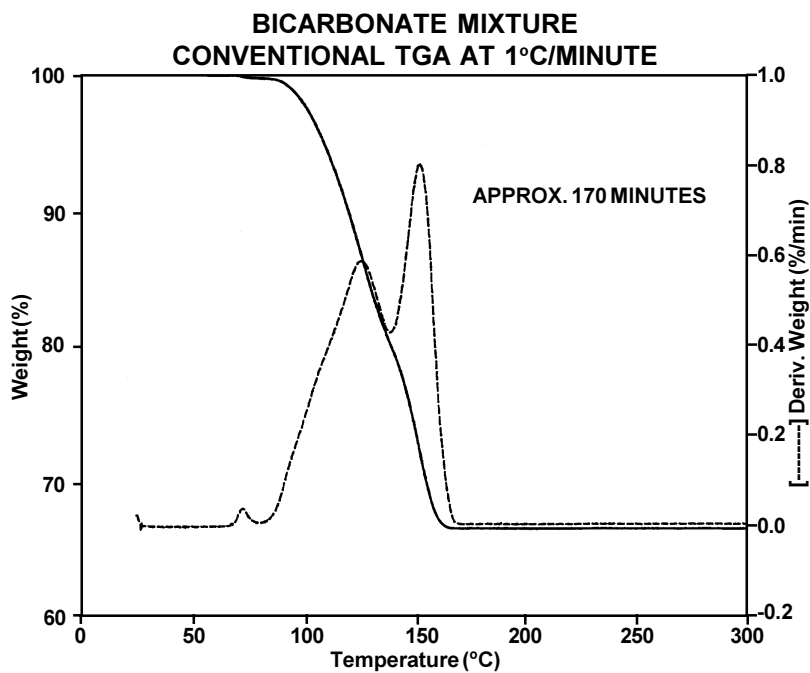
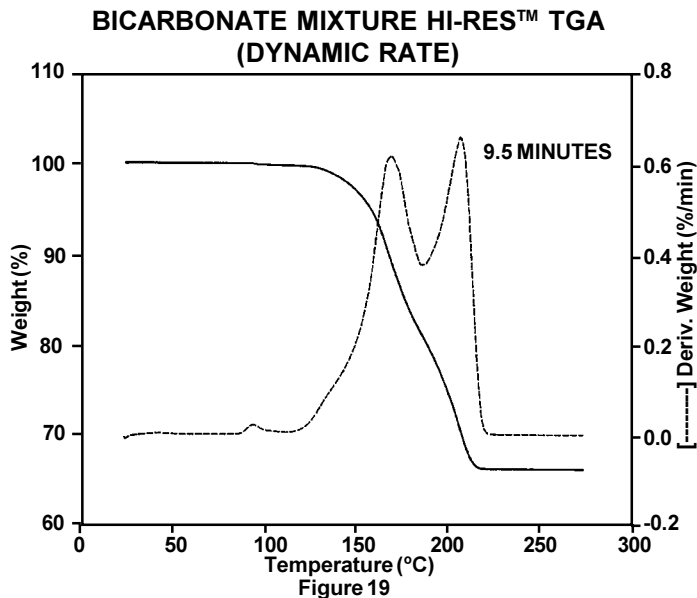


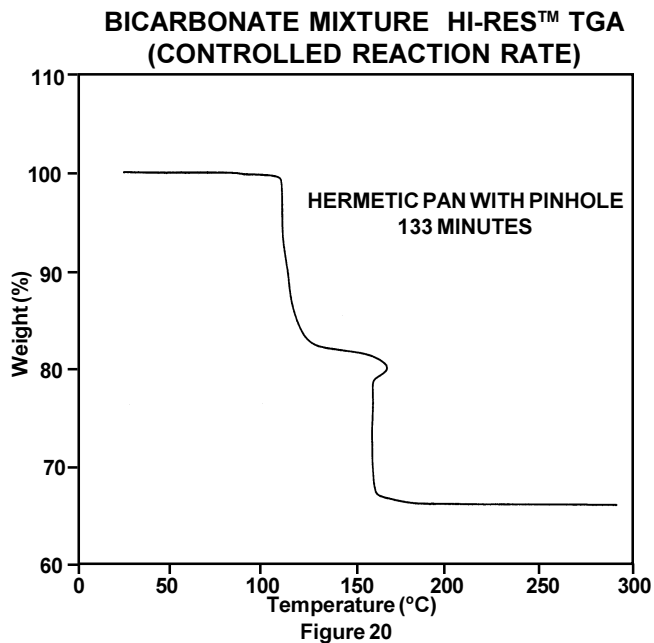
Figure 18



innovations from TA Instruments (former DuPont Thermal Analysis Instruments). It joins previous advances, which include dual sample DSC, differential photocalorimetry (DPC), dynamic mechanical analysis (DMA), and dielectric analysis (DEA), and provides further indication of TA Instruments' commitment to developing innovative new products and services that help thermal analysts solve their material characterization problems.

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4. J. Chiu, *Applied Polymers Symposia*, No. 2 25-43 (1966).



\*High resolution thermal analysis (includes high resolution thermogravimetric analysis) and "Hi-Res™ TGA" are concepts for which TA Instruments, Inc. has filed patent and trademark applications respectively.

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