APPLICATION NOTE

Thermal Analysis

Enhanced Separation of Components in ABS Polymer: Using AutoStepwise TGA

PerkinElmer Pyris 1 TGA

Introduction

One of the most important engineering thermoplastics is ABS whose important properties are derived from its three monomeric components – acrylonitrile, butadiene and styrene. Each of these components imparts a different and useful set of properties to the final resin. Acrylonitrile primarily offers chemical resistance and temperature stability while styrene yields rigidity and processibility and the butadiene supplies the ABS with toughness and impact resistance. ABS resins are used for a wide variety of engineering applications including automotive (panels, consoles, grilles and housings), appliances (door and tank liners, crisper trays, injection molded housings), building and construction (pipes), consumer (toys, shower stalls, lawn and garden products, furniture) and business (computer housings and consoles).

ABS resin is actually a two-phase system having a styreneacrylonitrile copolymer (SAN) as the main, continuous phase with a dispersed phase of butadiene rubber. ABS is sometimes considered to be the first polymeric alloy as the butadiene phase is compatibilized with the rigid SAN component through grafting.

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The ratio of the rigid SAN component to the butadiene rubber phase is critical, as it will significantly affect the resin flow/impact balance of the ABS resin. Increasing the level of the butadiene phase will increase the impact resistance and toughness of the resin, but at the expense of flow. The balance between resin flow and impact properties is a basic characteristic that distinguishes one ABS grade resin from another. For some applications, it may be desirable to have enhanced resin flow at the expense of impact resistance, while, for other applications, the most important consideration may be the resin's impact properties.

For these reasons, it is desirable to have a technique, which provides a means of quantifying the levels of the SAN and butadiene components in ABS resins. AutoStepwise thermogravimetric analysis (AS-TGA) provides such valuable data on ABS materials.

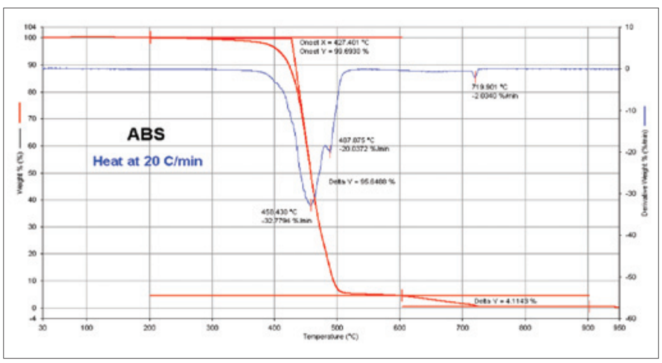

Figure 1. TGA results on ABS when heated at a constant rate of 20 ˚C/min.

Pyris 1 TGA and AutoStepwise Analysis

The PerkinElmer® Pyris™ 1 TGA instrument provides very high sensitivity and the ability to perform TGA experiments in the AutoStepwise isothermal mode. The use of the AutoStepwise mode gives the highest possible degree of resolution between successive decomposition events, such as those associated with complex, multi-component materials, including tobacco. With this technique, the sample is heated at a constant rate until the instrument detects amount of weight loss due to the evolution of volatiles or a decomposition product. The TGA will then automatically hold the sample under isothermal conditions and permits the given decomposition event to take place until the rate of weight loss is insignificant or less than the isothermal exit threshold value. The instrument will automatically resume heating the sample at a constant rate until the next weight loss event is detected. Using this approach, overlapping decomposition events can be fully separated or resolved.

The Pyris 1 TGA offers the following state-of-the-art features:

- Low mass, ultra-light balance for ultra-low noise and outstanding sensitivity
- Separate thermostatically controlled temperature environment of balance to provide highest possible stability
- Iris shutter assembly to isolate balance chamber from sample/furnace
- Automated ion stream to eliminate troublesome static effects
- High performance heat/sensor furnace technology
- Reduced furnace volume for more efficient switching of purge gases and elimination of oxygen during pyrolysis
- Autosampler accessory for unattended operation
- Accupik accessory for better handling of volatile samples without uncontrolled and unmeasured weight loss while waiting to run
- Environmental autosampler carousel to avoid exposure of queued samples to ambient air and moisture

Purpose

The purpose of this procedure is to demonstrate the ability of the AutoStepwise approach and the Pyris 1 TGA to provide separation and quantification of SAN and butadiene rubber components in ABS engineering grade resin.

Experimental

The following AutoStepwise experimental conditions were utilized to analyze the ABS resin:

Instrument:	Pyris 1 TGA
Mode of operation:	AutoStepwise isothermal
Heating rate:	50 ˚C/min
Auto step criteria:	Hold when rate of mass loss exceeds 1.25%/min Exit when rate is less than 0.10%/min Isothermal hold time of 10 minutes
Purge gases:	Nitrogen to 700 ˚C Oxygen from 700 to 950 ˚C
Gas switching:	TAGS (Thermal Analysis Gas Station)
Sample mass:	Approximately 13 mg

Results

Displayed in Figure 1 are the TGA results obtained when the ABS resin is heated under standard conditions, at a constant heating rate of 20 ˚C/min.

The TGA results show that the ABS resin undergoes thermal degradation at 427 ˚C with a total mass loss of 95.6%. Although the mass loss curve really shows no indication that two separate phases exist in ABS, the derivative trace (rate of mass loss) shows two peaks at 468 ˚C and 487 ˚C. The first peak corresponds to the degradation of the SAN copolymer, while the smaller peak at 487 ˚C is reflective of the decomposition of the butadiene rubber phase. However, it is not possible to easily quantify the amounts of SAN and butadiene present in this ABS resin because of the poor resolution or separation of the two transitions. The weight loss (4.1%) observed at 700 ˚C represents the oxidation of the fixed carbon as the purge gas is automatically switched from nitrogen to oxygen.

The resolution of TGA experiments can be improved by slowing the heating rate; however, this increases the overall experimental time. Displayed in Figure 2 are the TGA results generated on the ABS resin sample using a slower heating rate of 5 ˚C/min.

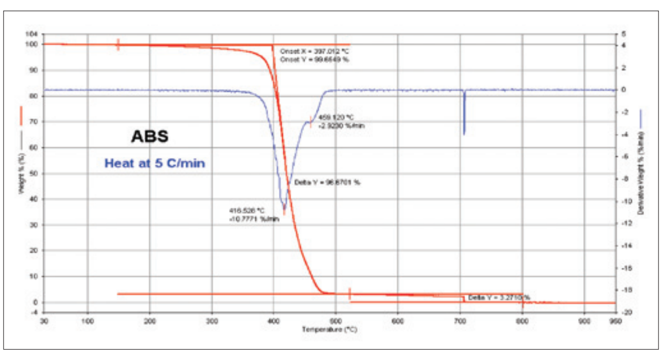

Figure 2. TGA results generated on ABS at a heating rate of 5 ˚C/min.

As these results show, there is an improvement in the resolution of the SAN and butadiene decomposition transitions as evidenced by a noticeable change in slope of the TGA mass loss data at about 470 ˚C. The change in slope reflects the differences in the rate of decomposition of the SAN and butadiene phases. However, it is still not sufficient enough to quantify the levels of the two components. And the experiment at 5 ˚C/min is 4 times longer than the TGA experiment conducted at the 'standard' rate of 20 ˚C/min.

The ABS resin was analyzed using the AutoStepwise approach and these results are displayed in Figure 3.

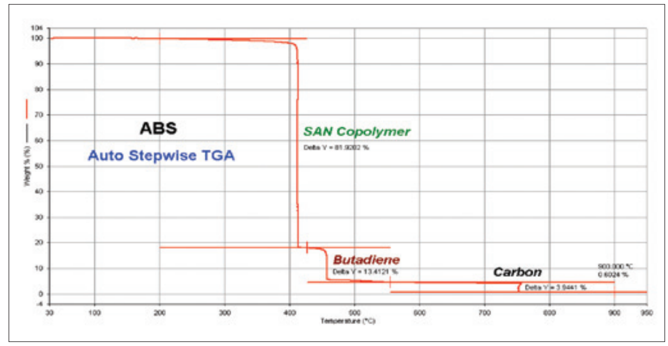

Figure 3. AutoStepwise TGA results obtained on ABS resin.

As these results demonstrate, the AutoStepwise approach provides outstanding resolution between the SAN copolymer and butadiene rubber components. The levels of the two phases in the ABS resins can be quantitatively assessed using the AutoStepwise approach. For this particular engineering grade ABS, there is 81.9% of the SAN copolymer and 13.4% of the butadiene phase. The level of fixed carbon present is 3.94% and the inert ash that remains at 950 ˚C is 0.60%. The AutoStepwise approach allows the thermal analyst to precisely measure the balance between the SAN and butadiene phases for the resin and this is critical to ensure that the resin exhibits the desired flow (SAN phase) and impact (butadiene component) properties.

The AutoStepwise approach is time efficient in that the Pyris 1 TGA uses a fast heating rate of 50 ˚C/min between the successive mass loss events. The instrument then automatically slows down, to provide the necessary high degree of resolution, when a transition is encountered.

The Pyris 1 TGA yields excellent reproducibility as is demonstrated by the results presented in Figure 4 which displays three experiments conducted in the AutoStepwise mode on the ABS resin.

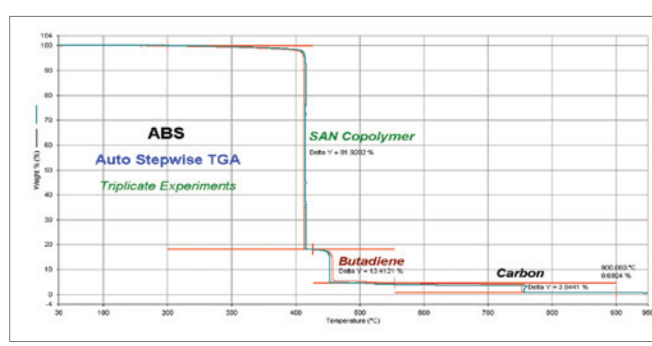

Figure 4. Triplicate AutoStepwise experiments performed on the ABS resin.

Conclusion

The Pyris 1 TGA instrument provides the AutoStepwise isothermal mode of analysis which yields the highest possible resolution between successive decomposition events. Complex, multi-component materials (polymers, elastomers, pharmaceuticals, foods) are best characterized using the AutoStepwise TGA mode. For the ABS engineering grade resin, the AutoStepwise approach was able to completely resolve and quantify the levels of SAN copolymer and butadiene components present. This is important since the end use properties of ABS resins (flow and impact resistance) are very dependent upon the levels of these two phases.

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