APPLICATION NOTE

Thermal Analysis

PerkinElmer Pyris 1 TGA

Compositional Analysis of Tire Elastomers using AutoStepwise TGA

Introduction

One of the main characteristics of elastomeric materials is their composition, which includes:

- Oil or plasticizer
- Polymer
- Carbon black
- Inert fillers

The particular end-use application of a given elastomeric material will determine the nature of its specific composition. The levels of the various components will have a major effect on the resulting end-use characteristics of the elastomer.

The multi-component nature of elastomers requires exacting analytical procedures, which can be used to provide both quality assurance as well as R&D information to manufacturers and users of the elastomeric products. Thermal analysis, and in particular thermogravimetric analysis (TGA), provides valuable information regarding the composition of elastomers.

TGA measures the weight loss (or gain) of a material as it is heated or held under isothermal conditions. Various purge gases (inert, oxidizing or reducing) can be used with TGA for more complete characterization purposes. PerkinElmer offers a variety of high performance TGA instruments to cover a wide range of applications and needs.

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In order to provide better separation of the oil or plasticizer in the elastomer, the following techniques have been used[1]:

- Isothermal analysis at a temperature significantly below the temperature at which the polymer will thermally degrade
- Use of a reduced pressure (or vacuum) to aid in the volatilization of the oil
- Extraction of the elastomer to physically remove the oil before the TGA measurement

The last two approaches are tedious and labor-intensive, which is a major drawback for quality assurance applications where efficiency and ease of measurement are major concerns.

The isothermal TGA method permits excellent separation of the oil from the polymer without having to resort to vacuum or extraction techniques. In the past, an 'ideal' temperature program had to be developed for each different elastomeric material in order to provide the best possible separation of the oil and polymer. Different oils will evaporate from the elastomer at different temperatures requiring the 'tuning' of the temperature program.

A better approach is the AutoStepwise isothermal method, which is a subset of the CRTA (controlled rate thermal analysis) technique as developed independently by Rouquerol[2] and Paulik and Paulik[3]. With the AutoStepwise approach, the sample is heated at a constant rate and, when a significant weight loss is detected, the TGA instrument automatically holds the sample under isothermal conditions. Once the rate of the mass loss becomes very small, the TGA automatically resumes heating the sample until the next significant weight loss event is encountered. Using this AutoStepwise approach, the TGA will automatically provide the best possible separation of the various components for elastomers, as well as other multi-component materials.

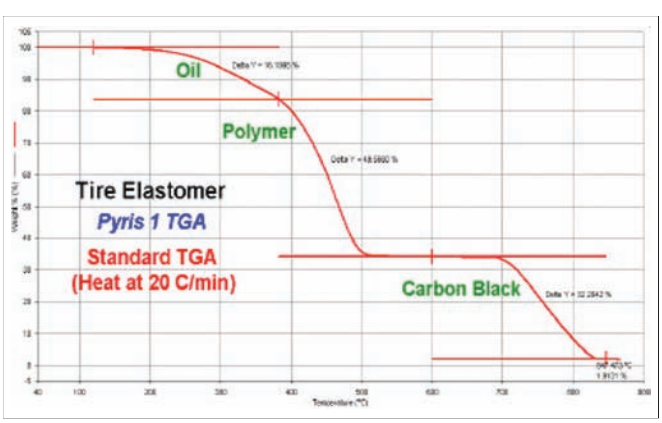

Figure 1. Standard TGA results obtained on tire elastomer by heating at a constant rate of 20 ˚C/min.

In this study, the AutoStepwise approach was used with the high performance Pyris™ 1 TGA to determine the composition of a tire elastomer.

Experimental

The following experimental conditions were used to characterize the compositional properties of the tire elastomer.

Experimental Conditions	
Instrument	Pyris 1 TGA
Method	AutoStepwise
Heating rate	20 ˚C/min from 30 to 900 ˚C
AutoStepwise Entrance Threshold	4%/min
AutoStepwise Exit Threshold	0.5%/min
Pan	Open platinum pan in ceramic holder
Purge gases	Nitrogen to 700 ˚C and air to 900 ˚C (30 mL/min)
Sample mass	Approximately 13 mg

Results

Displayed in Figure 1 are the TGA results obtained on the tire elastomer using the conventional TGA approach. These results were generated by heating the sample at a constant rate of 20 ˚C/min (not AutoStepwise). The purge gas was changed from nitrogen to air at 700 ˚C using the Thermal Analysis Gas System (TAGS)

The traditional TGA results on the tire elastomer shows that there is a severe overlap in the weight losses between 200 and 500 ˚C. The first weight loss at about 300 ˚C is that of the oil and is not decomposition, but the evaporation or volatilization of the oil. The weight loss occurring at about 450 ˚C is the thermal degradation of the polymer. Because of the relative slowness of the evolution of the oil, its weight loss runs into that of the polymer degradation. It is difficult to clearly define the levels of oil and polymer in the elastomer due to the severe overlap of these two transition obtained by standard heating TGA.

A much better alternative is AutoStepwise TGA where the TGA automatically detects the weight losses of the oil and polymer. The Pyris 1 TGA automatically holds the elastomer under isothermal conditions while the oil is evaporated and the polymer thermally degrades. Using this approach, excellent separation is easily obtained for the oil and polymer weight loss steps.

Displayed in Figure 2 are the AutoStepwise TGA generated on the tire elastomer sample.

The AutoStepwise results on the tire elastomer now show that excellent resolution is obtained between all of the weight loss events, including the difficult oil and polymer steps. The AutoStepwise TGA approach permits better quantitative compositional analysis of the elastomer. The results shown in Figure 2 yield the following compositional information on the tire elastomer:

- Oil = 21.8%
- Polymer = 43.9%
- Carbon black = 32.2%
- Inert filler = 2.11%

One advantage of the AutoStepwise TGA approach over the variable heating rate (High Resolution TGA) method is that the AutoStepwise handles diffusion controlled weight loss steps much better. The variable heating rate approach tends to move through the oil weight loss step much quicker, not providing the full evolution of oil before the polymer degradation step is encountered.

The AutoStepwise approach has very good reproducibility and this is demonstrated in Figure 3, which shows the AutoStepwise results obtained on 5 separate experiments on the tire elastomer.

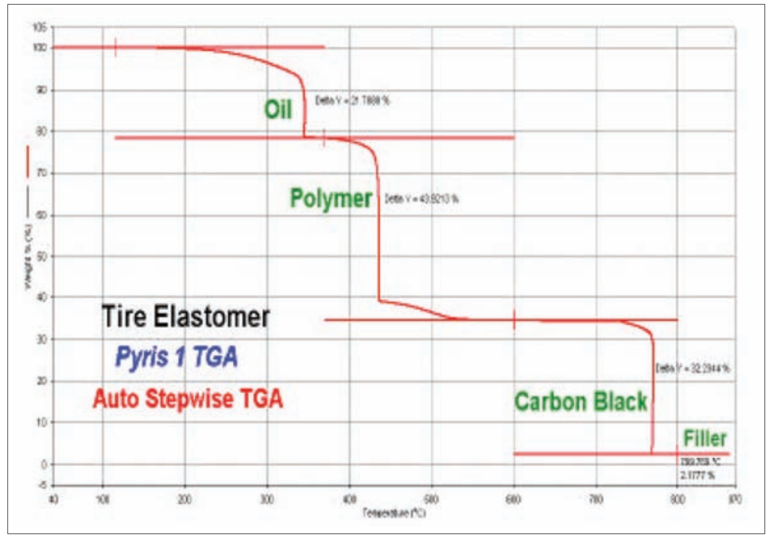

Figure 2. AutoStepwise TGA results on tire elastomer.

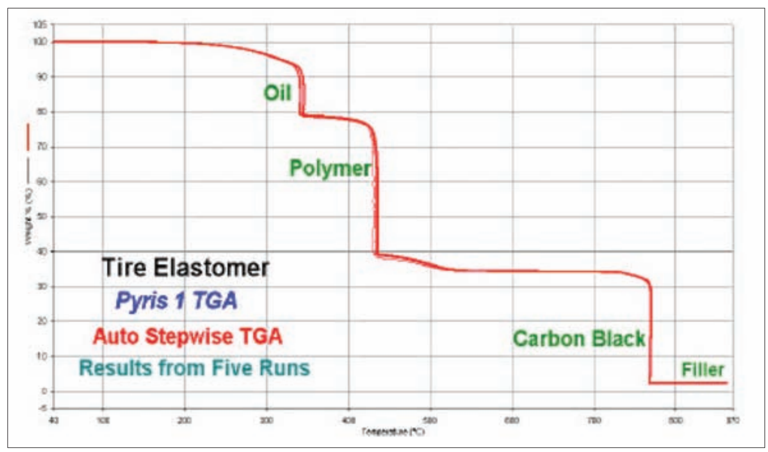

Figure 3. AutoStepwise TGA results from 5 experiments on elastomer.

Summary

The AutoStepwise TGA approach, featured with the PerkinElmer high performance Pyris 1 TGA, provides the best possible resolution, or separation, of weight loss events. For elastomers, the technique permits the quantitative separation of the critical components: oil, polymer, carbon black and inert filler.

References

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2. Rocquerol, J., *Bull. Soc. Chem.,* **31** (1964).
3. Paulik, F. and Paulik, J., *J. Anal. Chem. Acta,* **13,** 429 (1978).

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