APPLICATION NOTE

NEXTA STA200 / 200RV

Thermal analysis of rubber

INTRODUCTION

Rubber is a versatile polymer that has thousands of uses today. Natural rubber is made from latex that is extracted from trees and this form of rubber has been in use for centuries. For some applications synthetic rubber is used, especially within the chemical or petroleum industries. Both types of rubber are mixed with fillers and additives to achieve specific properties.

The properties of rubber, such as elasticity, water resistance and ability to mold into different shapes had led to thousands of applications, including rubber bands, printer rollers, thermal insulation and hose pipes. It is used as the basis for adhesive and lining reservoirs. The largest uses of rubber today, however, are tires and tubes.

As a polymer, rubber can be processed to give it different properties. Through vulcanization, the polymer chains can be shortened which makes the material stronger and harder. Other properties, such as abrasion and tear resistance, elasticity and specific gravity, can be fine-tuned through vulcanization and adding other compounds such as vegetable oils and waxes. Other elements such as zinc oxide and carbon black are added to act as fillers and reinforcing agents. And different rubbers can be mixed within components. Identifying the presence of these different rubbers and additional elements within the material is essential to ensure good quality control.

Differences in characteristics due to different types of rubber and additives, the ratio between polymer content and additive content, and percentages of respective types of rubber in mixed rubbers can all be determined by measuring thermal decomposition behavior using the NEXTA STA200 simultaneous thermogravimetric analyzer from Hitachi High-Tech. The NEXTA STA range is ideal for this application thanks to its unsurpassed baseline stability and sensitivity, and rapid gas purge.

Hitachi High-Tech Analytical Science's family of thermal analyzers have been employed in the field for more than 45 years, delivering world-class performance for precise materials characterization measurements, such as rubber analysis.

HITACHI INSTRUMENTS FOR THERMAL ANALYSIS OF RUBBER

NEXTA STA200/ NEXTA STA 200RV

The Hitachi NEXTA STA200 is ideal for fast and accurate rubber composition verification through finely tuned thermal analysis. An unsurpassed level of baseline stability, world-class sensitivity and advanced TGA and DSC capability ensures that the NEXTA STA200 slots easily into rubber development and quality control programs.

Available in two configurations, the 200 and the 200 RV version that includes our unique RealView technology, the NEXTA STA delivers most advanced TGA and DSC applications within a single instrument, including determining minute changes of weight, rubber decomposition, gasification and oxidation. The NEXTA STA200 has a baseline sensitivity of less than 10 µg and includes automation features with advanced software for easy and fast operation.

Several technological developments contribute to the NEXTA STA200's low level of baseline drift and stability. Firstly, the design of the balance makes it less susceptible to floating effects due to the purge gas. Floating effect (or buoyancy effect) is observed in TGA with vertical design. It causes baseline shift due to the heated gases pushing on the sample and make it look lighter. It is important to avoid this effect as it reduces the precision and accuracy of the measurements. Secondly, built-in thermogravimetry (TG) correction technology monitors changes in the reference sample and subtracts them from the sample readings to cancel out any drift due to expansion under high temperature. The balance unit is also held at a constant temperature to reduce environmental effects as much as possible.

RAPID ANALYSIS OF RUBBER WITH ENHANCED GAS-PURGE AND AUTO-SAMPLER FEATURE

The thermal analysis of rubber often requires measurements with a nitrogen atmosphere and in air. The NEXTA STA200 has advanced gas replacement technology to make the transition from the inert atmosphere to air as fast and efficient as possible. The instrument has an auto-sampler option that allows for automatic analysis of several samples at once. The NEXTA STA200 also includes the following to support rapid analysis:

- Up to four mass flow controllers can be chosen for running experiments under multiple purge gases
- Rapid purging of residual gases for accurate and fast carbon black analysis
- Built-in software guidance function makes the NEXTA STA very easy to use
- View changes your sample (such as changes in dimension, colour etc.) in real-time with the RealView camera system option

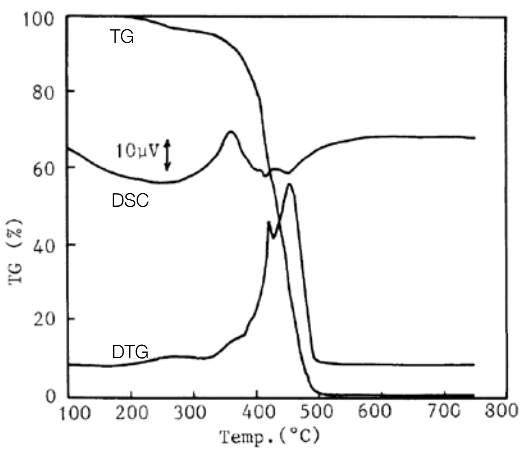
PERFORMANCE AND RESULTS

In this series of measurements, the Hitachi NEXTA STA200 analyzer was used to determine the composition of different types of rubber. Four different types of rubber were tested: SBR (styrene butadiene rubber), NR (natural rubber), CR (Chloroprene rubber), and SBR-CR mixed rubber. In each case, the temperature was taken from room temperature to over 700ºC. Results of each analysis are presented below.

SBR (styrene butadiene rubber)

The thermogravimetric curve that plots weight as a percentage of the starting weight shows that the SBR sample lost 99% of its weight once the temperature reached 500ºC. From this we can conclude that 99% of the sample is made from rubber polymers and softeners. The remaining 1% is made up of vulcanizing agents, such as sulfides, and metallic compounds added as catalysts.

The DSC curve gives us information on the reactions occurring within the sample. From the graph we can see an exothermic peak at 360ºC. This can be attributed to the recombining of the butadiene after breaking up of the polymer chain. The endothermic peak is due to the decomposition and gasification of the sample.

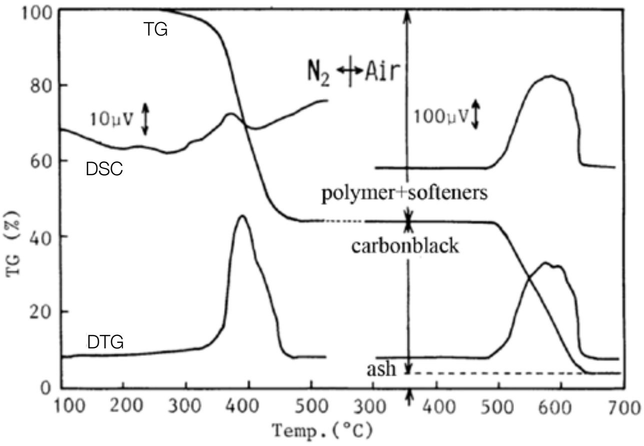


Sample weight : 15mg
Heating rate : 10ºC /min
Atmosphere : N_2, 250ml/min

Figure 1 STA curves of SBR (styrene butadiene rubber)

NR (natural rubber)

For analyzing natural rubber, the measurement was first carried out in a N2 atmosphere up to 550ºC, then the temperature was dropped to 300ºC and the gas flow was changed to air before taking the temperature up to 700ºC. The TG curve in N_2 shows that the natural rubber sample lost 56% of its weight at 550ºC. This is due to the decomposition and gasification of the polymer and softeners. When heated in air, the sample lost 40% of its weight and exhibited a strong exothermic peak between 500 - 630ºC. This is due to the oxidation and decomposition of carbon black, which was added to the natural rubber as an extender.

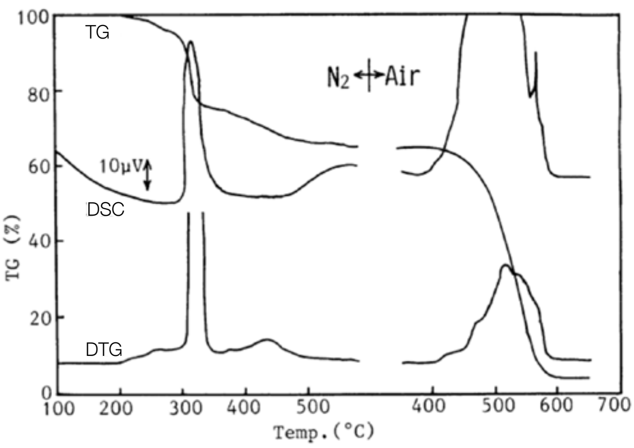


Sample weight : 15mg
Heating rate : 20ºC /min
Atmosphere : N_2(R.T.— 550ºC), 250ml/min
Air (300ºC — 700ºC), 250ml/min

Figure 2 STA curves of NR (natural rubber)

CR (chloroprene rubber)

Analysis within a nitrogen atmosphere shows a loss of weight with an exothermic reaction at around 330ºC. We can assume that this is due to the dehydrochlorination of the CR sample. Analysis within an air atmosphere shows the decomposition and oxidation of carbon black between 400ºC and 600ºC.

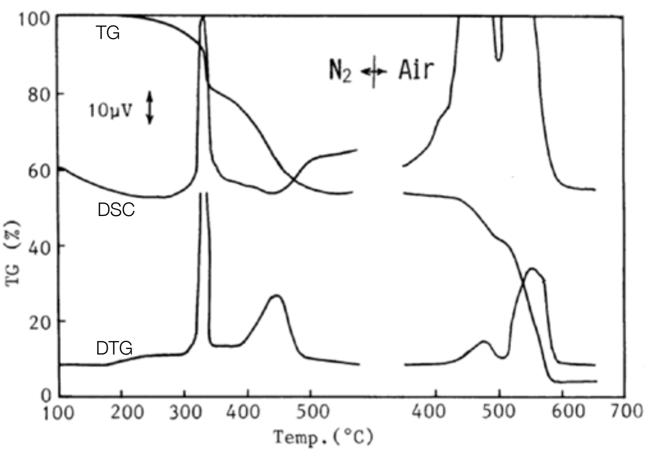


Sample weight : 15mg
Heating rate : 10ºC /min
Atmosphere : N_2 (R.T.— 550ºC), 250ml/min
Air (350ºC — 650ºC), 250ml/min

Figure 3 STA curves of CR (chloroprene rubber)

SBR-CR mixed rubber

This measurement shows how the NEXTA STA can be used to determine the constituent ratios of the different elements within mixed rubber. The weight loss of the CR element due to dehydrochlorination was used to calculate the CR content. From the graph you can see the loss of weight within a nitrogen atmosphere at 330ºC is 26.9%. This equates to a CR content of 54.7%.



Sample weight : 15mg
Heating rate : 10ºC /min
Atmosphere : N_2 (R.T. — 550ºC), 250ml/min
Air (350ºC — 650ºC), 250ml/min

Figure 4 STA curves of SBR-CR mixed rubber

RESULTS

1 The effects of heat treatment on PP crystallinity

Figure 1 shows the DSC curves for measurement condition 1. All samples showed an endothermic peak due to PP melting around 160°C. Furthermore, on the low temperature side of the endothermic peak, the untreated sample showed a smooth DSC curve between 110 and 125°C while the treated samples showed a minute peak.

Figure 2 enlarges the results around 120°C. The treated samples showed minute endothermic peaks of several tens of μW near their heat treatment temperatures. Each heat treatment temperature produced a different crystal structure. The peaks in the figure are considered the melting points of these structures during DSC measurement.

2 Measurement of isothermal crystallization

Figure 3 shows the DSC curves for measurement condition 2. PP crystallization produced an exothermic peak at each holding temperature. The lower the holding temperature, the sharper the peak and the earlier the peak top occurred. The higher the holding temperature, the broader the peak and the later the peak top occurred. This occurred because the higher the temperature, the greater the freedom of molecular motion, which makes crystallization more difficult and increases the time required for crystallization to be completed. The relation of crystallization temperature and crystallization time can be investigated using these results.

SUMMARY

These experiments show how the **NEXTA STA200 / 200RV** can be used to quickly and effectively analyze rubber samples. The efficient gas exchange mechanism ensures rapid switching between nitrogen and air atmospheres, and the excellent baseline stability and sensitivity ensures accurate quantification of rubber mixes and additives.

Many applications have been optimized for Hitachi High-Tech Analytical Science's thermal analyzers. For more information on other applications, please contact our experts at **contact@hitachi-hightech.com**.

NEXTA STA: COMPLETE QUANTITATIVE THERMAL ANALYSIS

Designed for complete thermal analysis of materials, including thermal resistance, decomposition temperature, melting point and specific heat testing, the NEXTA STA combines DSC and TGA to deliver TGA applications and more within a single analyzer.

The NEXTA STA offers:

- Ultimate accuracy and precision even when measuring trace amounts of material
- Superior heating technology that meets the most advanced applications of TGA
- Cp measurement in a wide temperature range
- Unique, Real View camera system for viewing material behaviour on screen
- Easy to use with automated features, intuitive software and simple report creation

Visit **www.hitachi-hightech.com/hha** for more information.