

# Competitive Analysis of the Rubber of Bicycle Tubes by Means of TGA-MS

Dr. Carolin Fischer and Jonas Rödel, Applications Laboratory Selb

### Introduction

Butyl rubber, a copolymer of isobutylene and isoprene, is the most commonly used material for the inner tube of a bicycle tire. Its benefits include a relatively low price, long service life and minimized air leakage. For optimized properties such as maximized flexibility and minimum rolling resistance, some additives are required at a low percentage amount. In this study, used bicycle inner tubes from two different manufacturers were analyzed with TGA to identify differences.

### Methods and Sample Preparation

Prior to the measurement, the samples were cut into several small pieces and placed into an open  $\text{Al}_2\text{O}_3$  crucible. The samples were heated in a nitrogen atmosphere to 850°C and in an air atmosphere from 850°C to 1100°C.

For the thermogravimetric investigation, the NETZSCH TG *Libra*® coupled to a QMS *Aëolos*® was employed. The measurements were carried out under the conditions detailed in table 1.

**Table 1** Measurement conditions

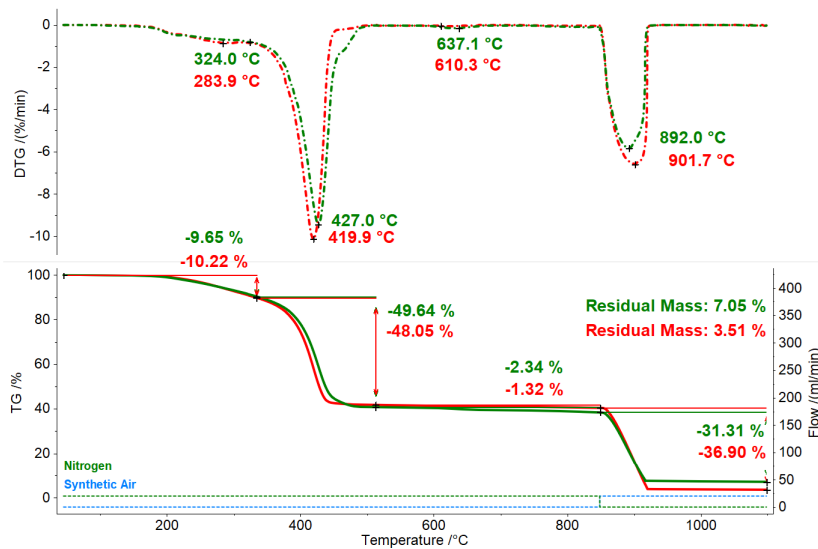
Sample mass	Manufacturer A (10.34 mg)	Manufacturer B (10.06 mg)
Crucible material	Aluminum oxide 85 µl, open	
Temperature program	40°C to 850°C in nitrogen, 850°C to 1100°C in air	
Heating rate	10 K/min	
Atmosphere	Nitrogen, air	
Gas flow rate	40 ml/min	
QMS	1 - 300 amu, Scan per mass: 20 ms	

## Results and Discussion

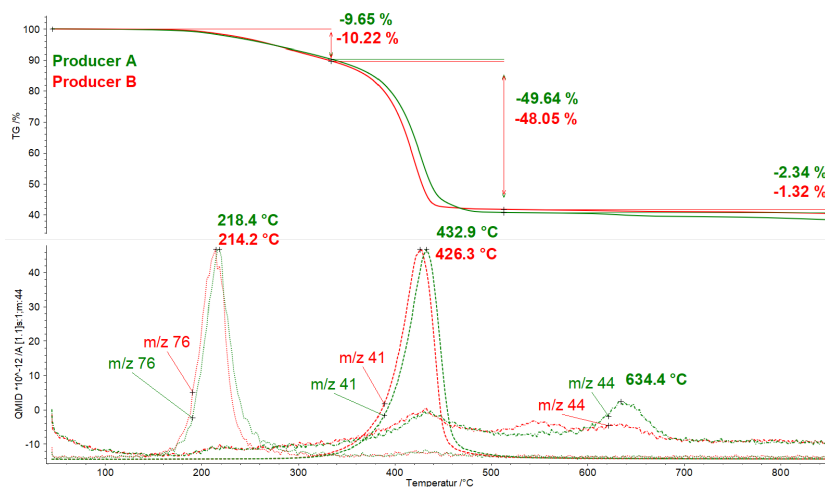
The resulting thermograms are depicted in figure 1. Under an inert atmosphere, both samples show three mass-loss steps. The first two mass-loss steps, between 200°C and 500°C, are associated with the decomposition of the rubber mixture. The rubber composition was probably different in these two samples, as slightly different percentages were detected, and the mass-loss rate (DTG) peaks were shifted. The third mass-loss step was caused by the decomposition of the carbonate filler. As different amounts of mass change were detected, different filler amounts were probably used.

Above 850°C, the air atmosphere caused the combustion of the residual carbon. The resulting residual mass corresponds to the ash content. Again, a specific difference was observed between the two samples, indicating a different amount of oxide minerals. The ash content of the sample from manufacturer B was about double the amount of that from manufacturer A.

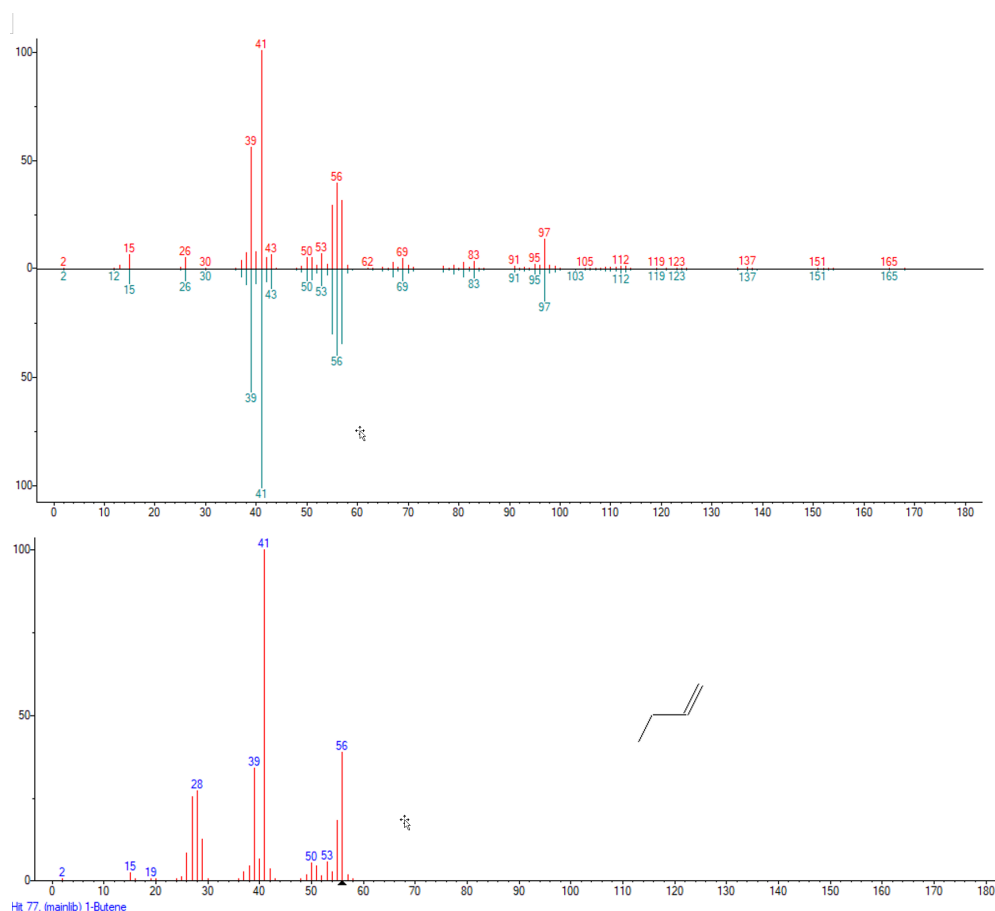
The evolved gases were additionally analyzed with the quadrupole mass spectrometer (QMS) connected to the gas outlet of the thermobalance. At 218°C (214°C), both samples showed an increase in mass number 76, which can be associated with the release of CS<sub>2</sub>, a vulcanization residue; see figure 2.



1 Temperature-dependent mass change (TGA) and rate of mass change (DTG) of both samples (manufacturer A = red; manufacturer B = green).



2 Temperature-dependent mass change (TGA) and ion currents m/z 41, 44 and 76 of both samples (manufacturer A = red, manufacturer B = green).



**3** (a) upper part: measured mass spectra at 420°C of manufacturer A (red) and manufacturer B (green)  
 (b) lower part: library spectrum of 1-butene

The detected mass spectra at 420°C show no significant difference for either sample, with  $m/z$  41 being the most intense fragment; see figures 2 and 3a. The measured spectra show high similarity to the main pyrolysis product of butyl rubber 1-butene<sup>1</sup>; see figures 3a and 3b.

At 634°C, the mass spectrometer detected an increase in  $m/z$  44 for the sample from manufacturer B, confirming the release of  $CO_2$  from carbonate decomposition. This indicates that a higher amount of carbonate filler was used in the sample from manufacturer B.

The release of the different mass numbers can be easily compared to the TGA curve in a temperature-dependent scaling; see figure 2.

### Summary

In conclusion, TGA-MS analysis enables detailed insight into the composition of two competitive inner tubes of bicycle tires. The thermobalance determines the thermal stability and allows conclusions to be drawn about the composition, such as the rubber content, filler content, carbon content and ash content. Even the smallest of differences could be identified. Simultaneously recorded mass spectrometer data facilitates the interpretation of the decomposition processes by identifying the gases released. The use and percentage of the respective additives and fillers are decisive for the quality of the tire; e.g., calcium carbonate also has a significant reinforcing effect on both natural and synthetic rubber, and can improve consistency. It also influences the dynamic properties of rubber.

<sup>1</sup> Pyrolysis GC/MS Data Book of Synthetic Polymers, Tsuge Shin, Ohtani Hajime, Watanabe Chuici, Elsevier, 2011