Comprehensive Investigation of PVC Floor by TGA-FT-IR and ATR

Dr. Carolin Fischer

Introdcution

PVC flooring is widely used in residential, commercial, and industrial settings due to its durability, versatility, and cost-effectiveness. Understanding the thermal behavior of PVC floor materials is essential for ensuring their optimal performance, safety, and longevity. Thermal analysis techniques provide valuable insights into the thermal properties and behavior of PVC floor materials.

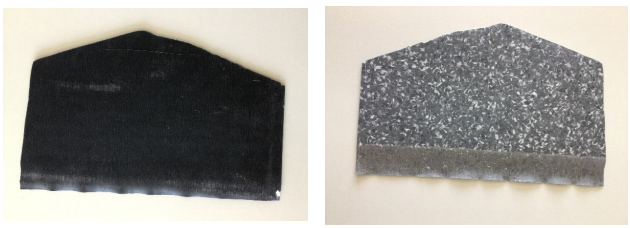
The distinct benefit of coupling thermal analysis with gas analysis lies in the ability to thereby characterize not only the thermal behavior but also the emission profile of PVC floor materials. By analyzing the gases evolved, it becomes possible to identify any out-gassing of toxic or harmful substances during heating, which can have implications for indoor air quality and human health. This information is particularly significant for applications where PVC floor materials are used in enclosed spaces, such as homes, offices, schools, or healthcare facilities.

Experimental

The combination of the Bruker *INVENIO* and the NETZSCH TG 209 ***F1*** *Libra*® offers a great variety of possibilities for analyzing polymers. Beyond routine TGA measurements, the combination with the *INVENIO* also allows for the investigation of solid samples by ATR (attenuated total reflection) in the internal compartment as well as the identification of the gases released during decomposition by the heated external gas cell. It is possible to alternate between measurements without any hardware changes, just by choosing another experiment in the software.

ATR Investigations

First, both sides of the floor sample were investigated by ATR by putting the complete sample onto the diamond crystal in the internal compartment and fixing it with the clamp. The IR beam penetrated the sample only by a few micrometres and therefore mainly detects the surface composition. The bottom of the sample was colored black and exhibited high similarity to a paint batch in the ATR spectrum (figure 2a) and b)).



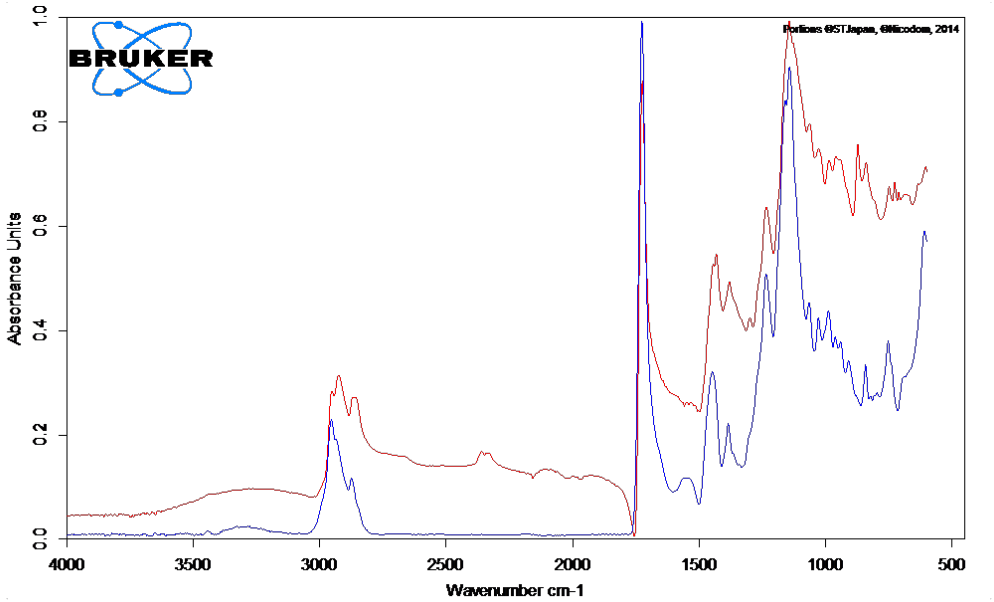
2 a) Bottom and b) top of the sample

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

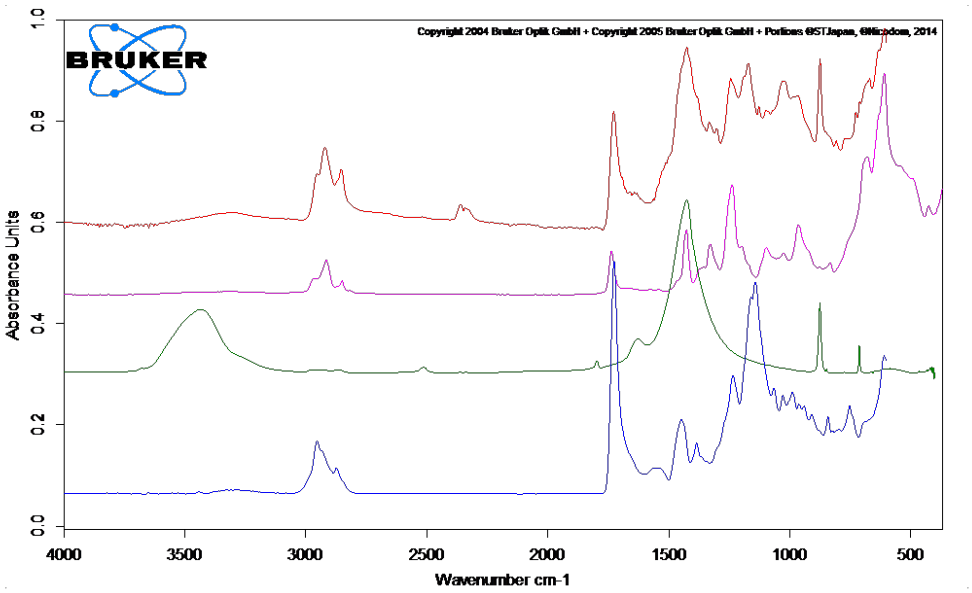
NETZSCH

The top of the sample showed several different colors. Therefore, the ATR spectra also depend on the position taken. One spectrum is shown as an example in figure 5. Here, a match with several different compounds was found, including PVC (pink), calcium carbonate (green) and paint (blue).

These first FT-IR spectra deliver the first part of the puzzle, analyzing the composition of the sample.



3 Measured ATR spectrum of the sample top (red) compared to a library spectrum of the universal paint (blue curve)



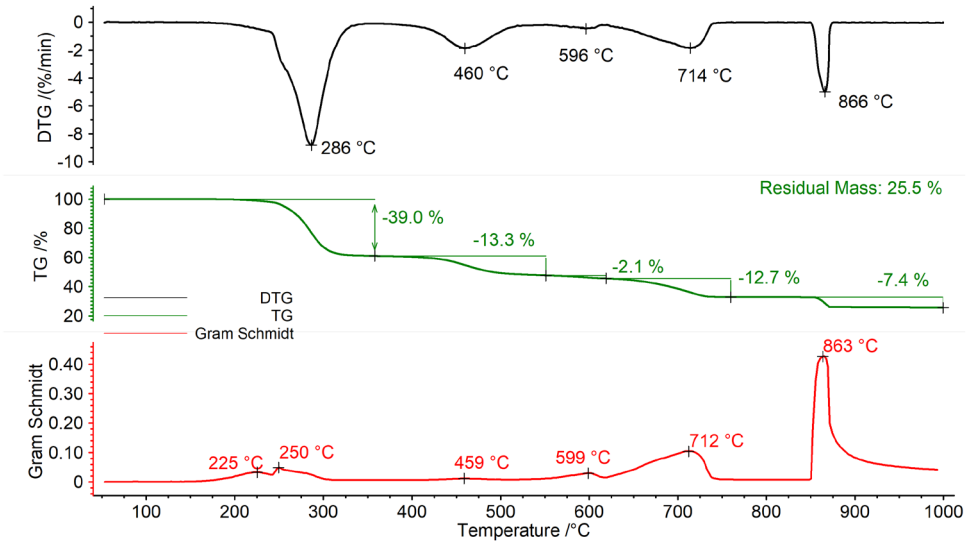
4 Measured ATR spectrum of the sample top (red curve) compared to a library spectrum of the universal paint (blue curve), $CaCO_3$ (green curve) and PVC (pink curve)

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

FT-IR-Results

Furthermore, thermal analysis by TGA-FTIR yields information about the thermal stability, the gases evolved during pyrolysis, the filler content, the carbon added and the ash content. Figure 5 shows the TGA curve after heating a small part of the sample (10 mg) in a nitrogen atmosphere to 850°C at 10 K/min. This heating resulted in four mass-loss steps of 39.0%, 13.3%, 2.1% and 12.7%. Above 850°C, air was used as a purge gas. In this heating segment, the residual carbon was burned and an ash content of 25.5% remained.

The Gram Schmidt curve displays the overall IR intensities and behaves as a mirror image of the mass-loss rate (DTG) while also showing maximum intensities during the mass-loss step. This proves that the evolved compounds interact with the IR beam.



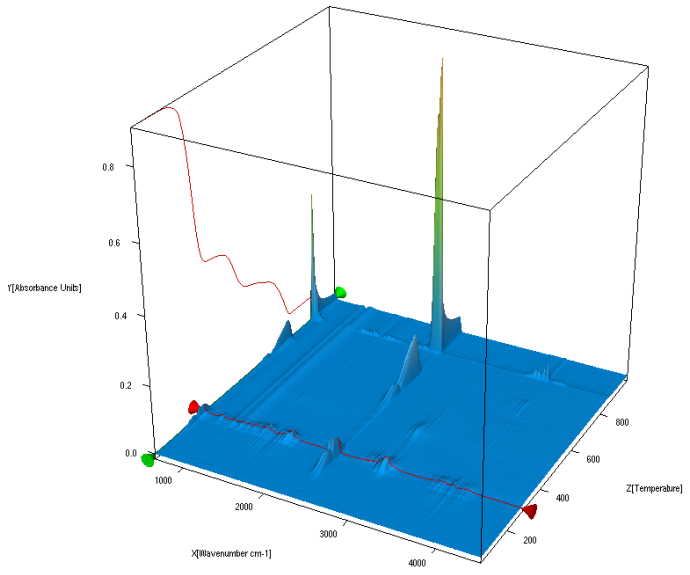
5 Temperature-dependent mass change (TGA, green curve), rate of mass change (DTG, black curve) and Gram-Schmidt curve (red) of the floor sample.

NGB · Application Note 288 · EN · 0723 · Technical specifications are subject to change.

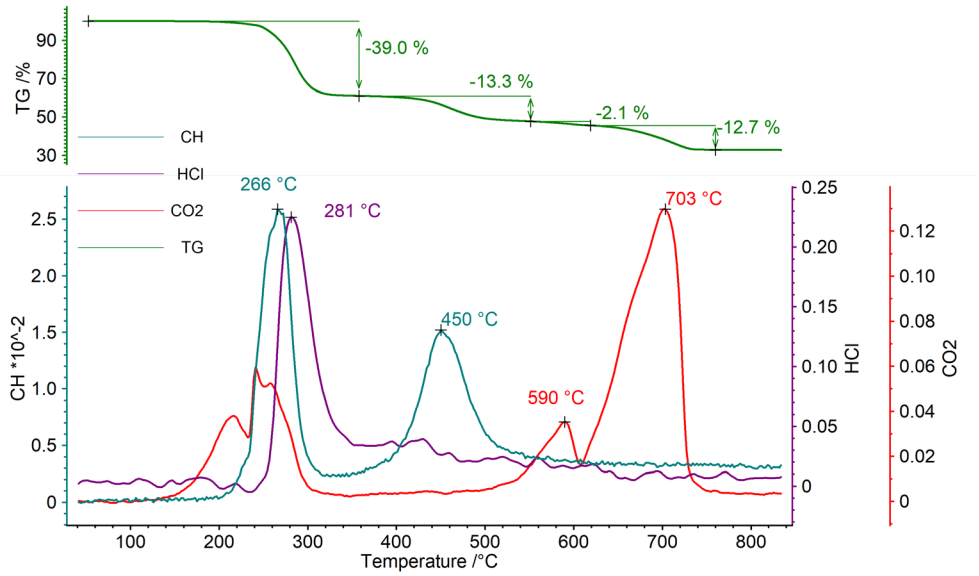
NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

The resulting FT-IR data can be seen in figure 6. The temperature- and wavenumber-dependent 3D plot shows a good correlation between the mass loss and the detection of IR-active gases. Single spectra were taken at each peak maximum in the 3D plot to identify the gases released. During the first mass-loss step, the release of water, CO_2, HCl and hydrocarbon fragments (identified by CH vibrations) was found. In correlation with the second mass-loss steps, mainly CH vibrations were detected.

These findings prove that the decomposition of the polymeric content took place between 200°C and 550°C. Between 550°C and 850°C, mass-loss steps three and four were accompanied by the release of carbon dioxide; see figure 7. As these reactions took place under an inert atmosphere, these effects are probably attributable to the decomposition of carbonate fillers such as $CaCO_3$. Since there are two mass losses in this temperature range, it is likely that a second carbonate was present in addition to $CaCO_3$ at a low concentration.



6 3D plot of all detected IR spectra of the floor sample; TGA curve plotted in red at the back of the cube.



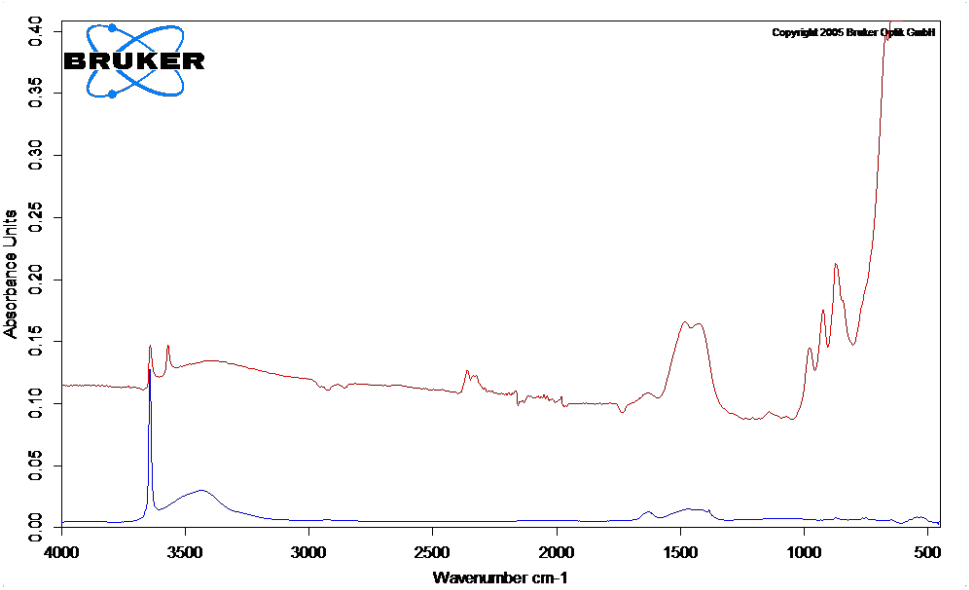
7 Temperature-dependent mass change (TGA, green curve) and the traces for CH vibrations (turquoise), HCl (purple), CO_2 (red) of the floor sample.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

According to the stoichiometric equation of the $CaCO_3$ decomposition, the original sample probably contained about 28.9% of $CaCO_3$. Above 850°C, the residual carbon was burned in an oxidizing atmosphere to CO_2. This carbon content may have originated from pyrolytic carbon and/or from added carbon black as a color agent.

Following the thermal treatment by TGA, the remaining residue was also analyzed by ATR in the internal compartment of the *INVENIO*.

Figure 8 shows the measured spectrum in comparison to the library spectrum of CaO, revealing some similarity. As CaO is the decomposition product of $CaCO_3$, a third hint was found that the original sample contained $CaCO_3$ as a filler.



8 Measured ATR spectrum of the sample residue (red curve) compared to a library spectrum of CaO (blue curve)

Conclusion

In conclusion, this comprehensive analysis of a relatively simple-looking floor sample carried out with the TGA-*INVENIO* coupling combined with ATR measurements revealed a number of interesting material properties. It was possible to analyze the thermal stability, identify the gases released during thermal decomposition, detect the type and amount of filler, and determine the ash content along with its identity.

NGB · Application Note 288 · EN · 0723 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com