NETZSCH

Applications Laboratory
Thermoanalytical Section

Thermal stability and decomposition behavior by mass changes and evolved gas analysis for KTX 30 product.

by
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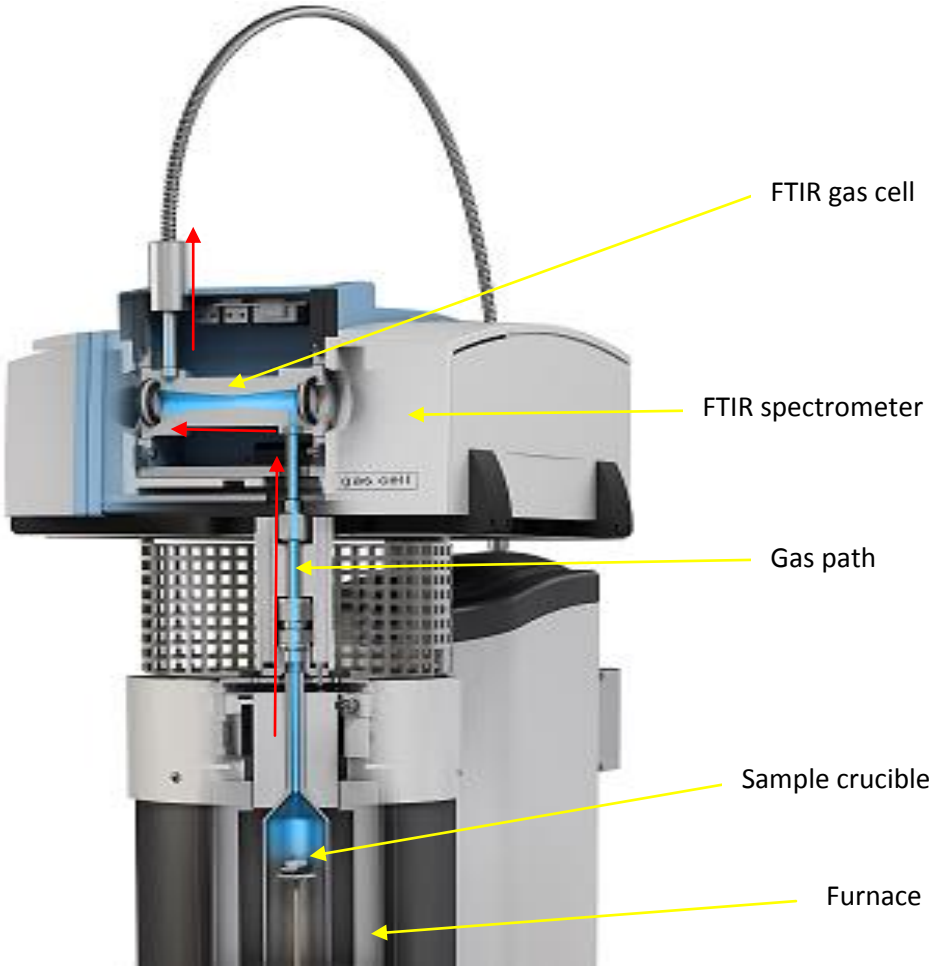
Introduction

The Thermoanalytical Section of the NETZSCH Applications Laboratory received KTX30 product sample from PHSC Chemicals Sp. z o.o. Poznań (Poland), for the measurement of the temperature dependent mass changes and evolved gas analysis.

The NETZSCH model STA 449 ***F1*** *Jupiter*® simultaneous thermal analyzer can be used to measure the mass change and transformation energetics of a wide range of materials. The top-loading STA can be equipped with various easy exchangeable TG, TG-DTA or true TG-DSC sensors and with different furnaces to accommodate different application areas. The system employed for this work was equipped with a rhodium furnace capable of operation from 25 to 1650 °C. The system is vacuum tight, allowing measurements to be conducted under pure inert, reducing or oxidizing atmospheres. Heating rates of up to 50 K/min can be employed and the digital resolution of the balance is 25 ng/digit. Data acquisition and evaluation, as well as instrument control, are carried out using a MS-Windows™ software package. The software allows the computation of the rate of mass change, mass change steps, onset and peak temperatures, inflection points, peak area integration, etc.

The gases evolved by thermal analysis are directly injected into the FT-IR spectrometer from Bruker Optics. The gas cell is heated to 200 °C and possesses a volume of 5.8 mL. The DTGS detector of the FT infrared spectrometer covers a rage of 600 cm^{-1} to 6000 cm^{-1}. Every spectrum is averaged from 16 scans. One scan takes around one second.

Data exchange between NETZSCH *PROTEUS*® software and Bruker *OPUS*™ software is done online during the measurement. This guarantees simultaneous start and stop of the measurement as well as data exchange during the measurement.



NETZSCH *Perseus*: Coupling of the NETZSCH STA 449 ***F1*** *Jupiter*® with the FT-IR spectrometer from Bruker Optics (scheme).

Experimental

Furnace:	SiC (1600C)
Sample Carrier:	TG/DSC (1750C)
Crucibles:	ceramic Al_2O_3 crucible; 85ul
	5,2 mm diameter
Sample Thermocouple:	Type S
Purge Gas:	oxidizing synthetics air (50 ml/min)
Protective Gas:	oxidizing synthetics air (20 ml/min)
Temperature Program:	30°C – 950 °C
Heating rate:	10 K/min
Sample Mass:	26,63 mg (after drying the solvent)

Results and Discussion

Sample preparation:

The liquid product KTX 30 was deposited in clean Al2O3 crucible. The crucible was left to dry in room temperature (about 25°C) for time about 8h. After solved evaporation the solid thin layer of the product on crucibles walls was detected. Mass of the deposited layer of the resin was terminated by the very precise microbalance with accuracy of 0,01mg. The sample prepared in this way was subjected to controlled heating in the Netzsch STA 449 F1 device. The sample was deprived of the solvent on purpose, because a strong endothermic evaporation process of solvent could override the temperature range in which the sample is going to decompose. In addition, a large amount of solvents could ignite during heating in air, which could cause additional degradation of the tested resin layer. Therefore, the sample was measure in such a form as it occurs after depositing on a given surface under real conditions.

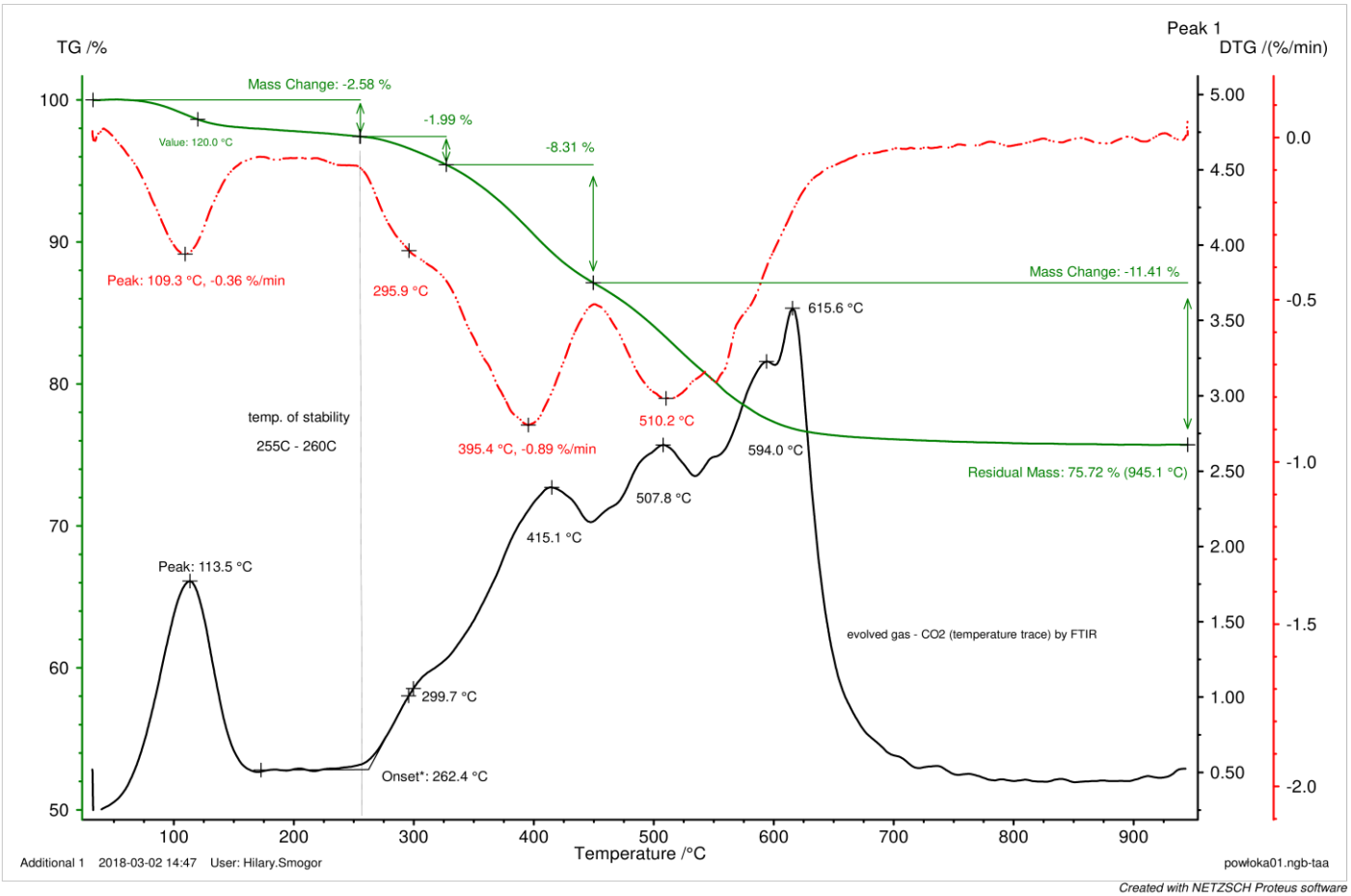


Figure 1 depicts the TG/DTG - FTIR results of sample.

The figure 1 presents - dependence of the TG curve (green), DTG (red) and intensity of evolved gas – CO2 trace (black) on temperature in Celsius scale.

TG curve depictures decomposition behavior of measured sample, we can observe that in accordance with the temperature increase, the sample begins to lose on the mass, it can be seen that the decomposition process follows in many stages in the temperature scale. Subsequent components of the sample begin to decompose and transforms into the gas phase. The decomposition gas product can be measured by the FTIR spectrometer for identification. We can see several mass loss steps: -2.58%, -1.99%, -8.31% and finally -11.41%. DTG curve depictures the rate of mass change over the time. In other words how fast the sample loss of the weight, it means in this temperature regions where the DTG (first derivative of TG) is nearby 0 the sample becomes to be stable in temperature and time – no mass change. So the firs mass loss step -2.58% is related to evaporation process of residual solvent content. Probably the butyl acetate in this case did not evaporate completely in this complicated (compared to a flat surface, for example wall) geometry of measuring crucible. The evaporation of solvent process has maximum speed in 109.3°C temperature DTG. After that the sample behavior is stable until the next decomposition process. The next decomposition process begins at a temperature above approximately 255°C - 260°C. Above this limiting stability temperature a multi-stage decomposition process begins, at least three stages -1.99%, -8.31% and finally -11.41%. According with the product specification the main compound is the organics polysilazane resin (main component of the embedded layer of KTX 30 product), so in this case above 260°C the organics parts of the polysilazane starting to decompose in several different steps. Above the 700°C the organics part is completely decomposed and the depolymerization (no more molecular chains structure) in polysilazane is dome – no more mass lass steps. The residual mass about 75,72% contain only silazane molecules which are according to the literature very stable until even 1200°C mostly by the strong silicone (Si) and Hydrogen (H) bonding. A further temperature increase can result in crystallization of the amorphous material and the formation of silicon nitride, silicon carbide and carbon. The decomposition process can be described also by the data from FTIR spectrometer (black curve). On the picture we can see the evolving gas released from the sample – in this graph is CO2 carbon dioxide. The decomposition gas product from the sample can partly burn in oxidizing atmosphere forming the carbon

dioxide. So as we can see above 150°C is no CO2 released from sample until about 260°C when the organic part of the resin can released and partly burn, so we have increase of CO2 content again. It is the next prove that the organics polysilazane resin compound is stable until 260°C in this case.

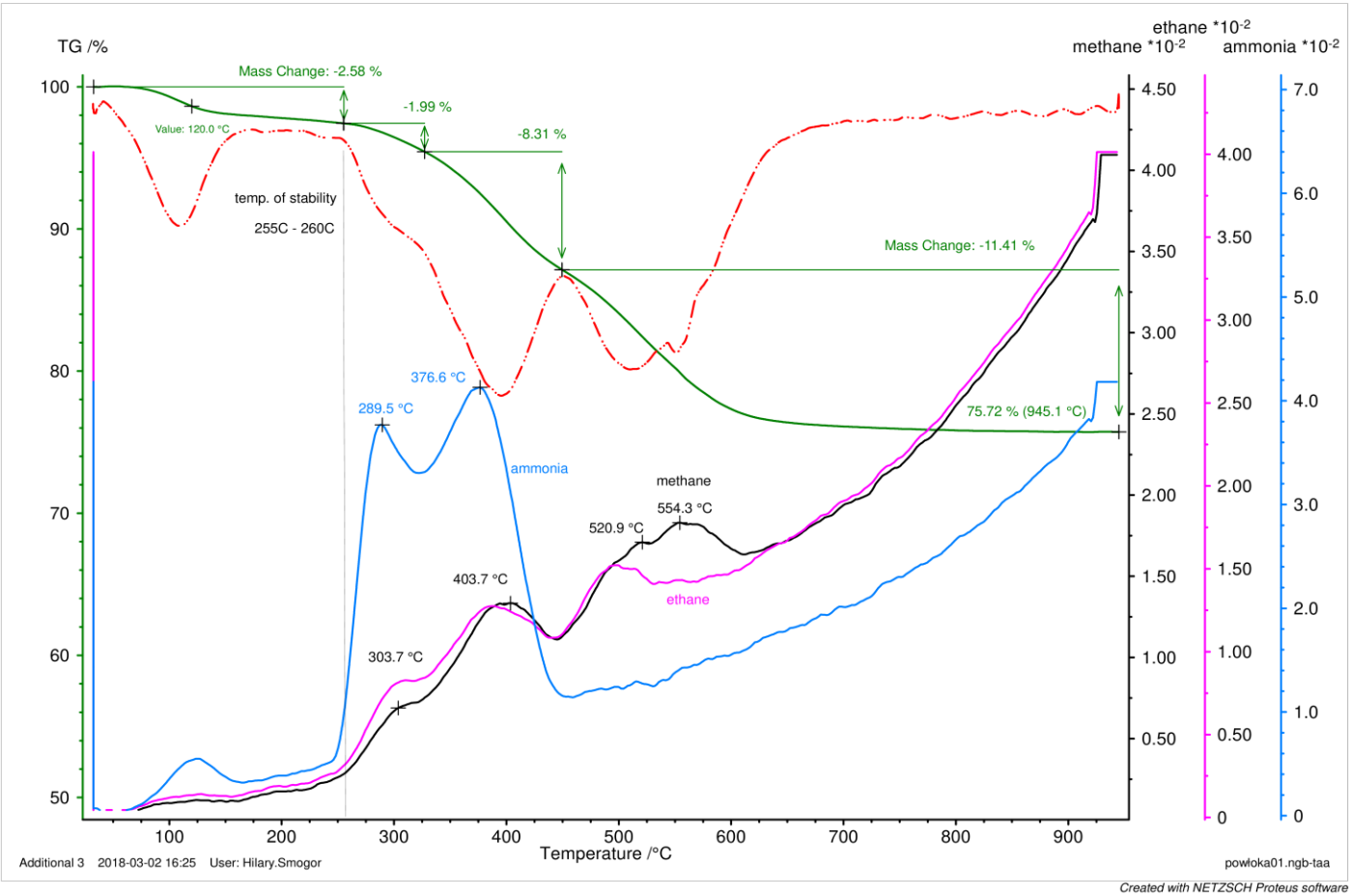


Figure 2 depicts the TG/DTG - FTIR results of sample.

The figure 2 is modification of figure 1 and depictures mostly the FTIR spectrometer data. In order to decomposition of organics polysilazane according with the literature above 100°C, further crosslinking of the molecules takes place with evolution of hydrogen and ammonia. I our case above 260°C, the organic groups (parts) of polysilazane decompose with the evolution of small hydrocarbon molecules (like ethane or methane **for example**), ammonia, hydrogen and trace of water. The figure 2 is experimental depicturing of describing situation. In last figure the correlation of “thermal data” and spectrometer data are connected in one 3D cube.

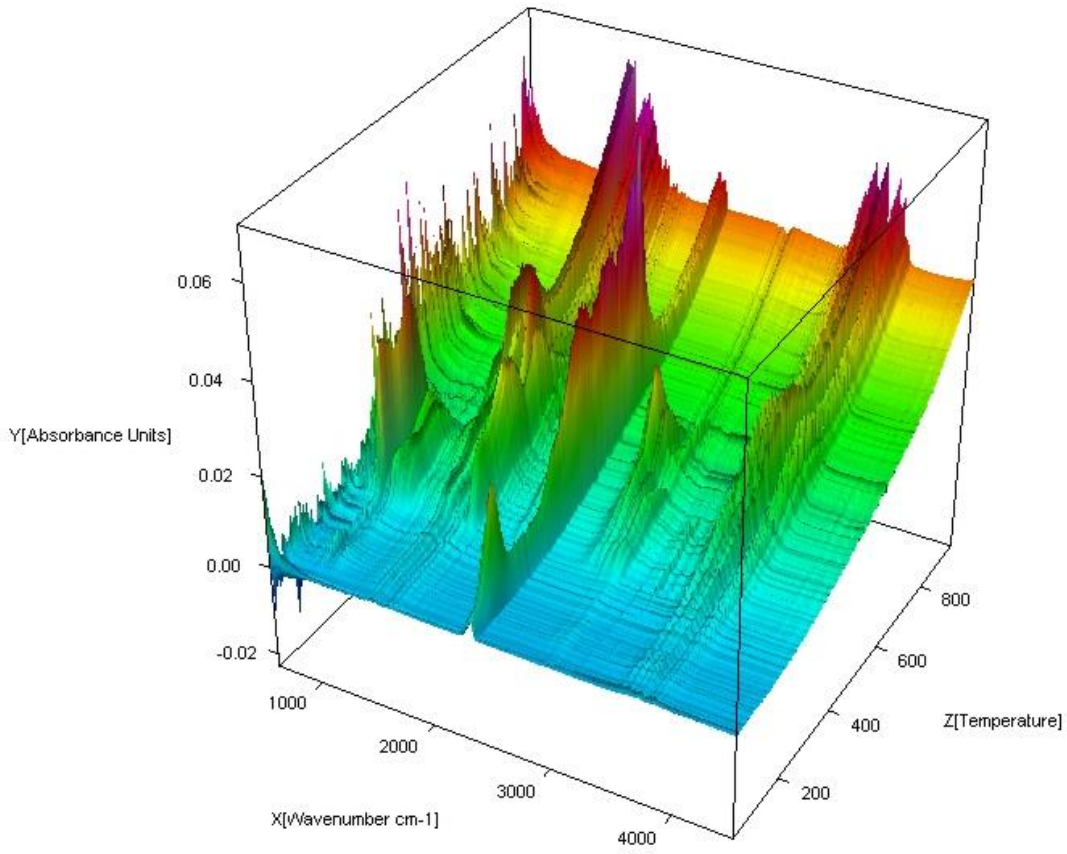


Figure 3: 3D plot of all detected IR spectra of sample in the temperature range 30°C to 950°C.

Picture 1 – Crucible after the measurements the residual mass in 950°C above 75% of initial mass.

Summary

The performed tests using the methods of Thermal Analysis and Infrared Spectrometry FTIR show that the embedded product KTX 30 based on organics polysilazane retains the complete thermal stability to temperatures around 260°C. Above this temperature decomposes the organic part of polysilazane - the main component of the test product mixture. In addition, increasing and maintaining the temperature above 110°C may resulting in an additional improvement in polymerization of the layer and additional cross-linking of the polysilazane resin - improving the consistency of the applied product layer.

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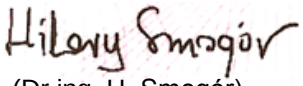

(Dr ing. H. Smogór)

(https://www.netzsch-thermal-analysis.com/en/)