Thermal stability and decomposition behavior by mass changes and evolved gas analysis for KTX 07 coating.

by

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Introduction

The Thermoanalytical Section of the NETZSCH Applications Laboratory received KTX07 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 range 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 Al₂O₃ 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 KTX 07 coating sample in liquid state was instilled at room temperature into pure ceramic (Al2O3 aluminum oxide) measuring crucible. The sample prepared in this way was measured without any delay. The initial weight of the sample the volatiles in the form of a solvent and the coating itself was determined by means of a precision microbalance with an accuracy of 0.01 mg. Then, the sample was given to the controlled heating in the furnace of the simultaneous thermal analyzer Netzsch STA 449 F1 at a rate of 10K/min in an oxidizing atmosphere - synthetic air.

Fig. 1 - dependence of TG, DTG curves and total intensity of gases released from temperature.

Figure 1 shows the relationship of the TG mass loss curve, the DTG mass loss speed curve (first TG curve derivative), and the analysis of the total intensity of released gases integrated in the spectrometer measurements depending on the temperature in the Celsius degree scale. The TG curve illustrates the process of decomposing the sample in the form of registering its mass losses as the
temperature rises. The heated sample begins to lose mass in various temperature ranges, characteristic for a given decomposition process (liquid or solid phases go to the gas phase). In many cases, such a process can be a multi-step process exactly as for the sample being tested. Gaseous decomposition products can be analyzed and identified by spectroscopic methods, inter alia FT-IR infrared spectrometry. In the case of the sample we can observe two expressions of weight loss: -44.78% and finally -47.38%. The mass remained at 900°C was 7.74% of the initial weight of the sample see figure 1. The DTG curve shows the rate of mass change for given decomposition levels. In other words, how fast the sample loses mass in a given temperature range. As you can see at the beginning, this speed increases, reaches the maximum and eventually decreases after the completion of a given stage of decomposition. In the temperature ranges where the DTG value approaches 0 (the graph is flat), the sample shows thermal stability - its mass is constant and we are before, between, or after the next decomposition process. In our case, the first loss of mass -49.78% is probably related to the evaporation of the solvent in any case liquid, later volatile part of the test coating. The minimum temperature on the DTG curve for this effect is around 136°C and the evaporation process is the fastest at this temperature. It can also be observed that near this temperature the FTIR spectrometer locally registers the highest intensity of the resulting gas phase (black curve). Above the temperature of about 200°C, the coating seems to be devoid of a liquid part, this is also indicated by a curve showing the integration of the signal coming from the detection of the released gases - the FTIR spectrometer does not register almost any gas released in addition to the carrier gas creating the measurement atmosphere. The above-mentioned temperature of the sample begins to be stable until another mass loss effect, which starts above about 400°C. Above this range, we can observe the beginning of the process of decomposition of the proper solid coating - remaining in the measuring crucible. This process is also clearly illustrated by the DTG curve with its subsequent minima. In other words, taking into account a certain reserve, it can be said that the limit of thermal stability of deposited coating under given conditions is about 380°C. The coating decomposition reaction proceeds fastest at a temperature of about 570°C - again the DTG curve. The end of the decomposition process can be taken at temperatures above 740°C. After a complete decomposition of the measured
coating, we can register a small residue above 7%. We did not find out in this study what kind of residue we have here to do.

In the course of the tests, an additional coating test was carried out (to be sure). This test was carried out on another sample also prepared in a different way. The liquid product KTX 07 was instilled into a pure ceramic (Al2O3 aluminum oxide) measuring crucible. The crucible was allowed to dry (evaporation of the liquid portion - volatile) at room temperature (about 25°C) for a period of about 3 hours. After evaporation of the volatiles, the remaining mass of the coating layer deposited on the walls of the crucible was determined by means of a precision microbalance with an accuracy of 0.01 mg. In addition, this method of sample preparation simulates the process of deposition and creation of the solid layer of the coating has a surface - as it happens with the real application of the coating.
Fig. 2 - dependence of TG, DTG curves and total intensity of released gases on temperature

In this approach, the study was subjected to a sample devoid of the (most of) its liquid phase. A sample that had a chance to bond to the substrate (embed) with its proper solid phase of the coating. The purpose of such a second test was to check whether it affects the thermal stability of the deposited coating. Such sample preparation simulates to a good extent a real situation in which we apply the test coat and wait for its evaporation and hardening on a given substrate.

As can be seen in Figure 2, the basic difference is the change in the ratio of the first and second mass losses steps. Of course, this is not surprising at all, the sample has had enough time to initially get rid of its liquid phase. We see that the first weight loss is now only about 9% of the total initial weight of the sample. So much, more or less, we can still have an unvaporated liquid phase in the tested coating. As can be seen with the further increase in temperature, it can be noted, similar as in the previous study, the behavior of the solid deposited coating. The actual (main) decomposition, as previously starts above about 400°C, and the coating itself retains, as before, thermal stability to about 380°C.

This behavior is also confirmed by the data from the FTIR detector of released gases, where the increase in the intensity of recorded gas decomposition products can be observed only after exceeding about 400°C. The maximum speed of the evaporation process of the liquid phase residues was recorded at a temperature of about 110°C, while the maximum speed of the solid phase decomposition process was recorded at a temperature of approximately 533°C - DTG curve see figure 2.

Figure 3 focuses on the separation of signals from the FTIR spectrometer, which records the spectra characteristic for different gases emitted at subsequent stages of decomposition of the sample measured in the liquid state. In other words, in the observed situation, the intensity of the FTIR spectrum characteristic for the detection of the liquid phase of the shell should increase and decrease in the "low" temperature range while the intensity of the spectrum characteristic for solid phase decomposition - the proper part of the coating should grow and decrease in the "higher" temperature range. Data from the FTIR spectrometer illustrates exactly this situation - fig. 3 blue and green curve. It can be seen that the liquid part stops
evaporating to about 200°C, while the solid part of the coating begins to decompose and turn clearly into gas, only slightly above 400°C.

Fig. 3 - dependence of TG, DTG curves and intensity of released gases for the liquid part and solid part from the temperature.
Fig. 4 - an attempt to identify the released gas for the liquid phase of the tested coating.

Figure 4 shows an attempt to adjust the FTIR spectrum recorded at the maximum evaporation temperature of liquid part of the coating - temperature around 140°C.

Fig. 5 - an attempt to identify the released gas for the solid phase of the tested coating.

Figure 5 shows an attempt to adjust the FTIR spectrum recorded at the maximum decomposition temperature of the solid part of the coating - temperature around 585°C.

The program containing the FTIR spectra database tries to match the spectra recorded during the experiment, the spectrum most similar in terms of the characteristic bands of a given spectrum and their individual intensities. Of course, like any database, it has some limitations in the form of the amount of different spectra for individual substances and that many of them represent measurements for a solid or liquid phase of a given substance. In our case, the measured FTIR spectra are characteristic, due to the type of apparatus (FTIR spectrometer), only for the gas phase of a given substance. Due to the facts cited, the identification of a given...
substance is rather general. The spectra from our experiment in both drawings are red fig 4 and 5. As far as the liquid phase is concerned, its spectrum is compared to the base in Figure 4, and the identification generally indicates hydrocarbon-based solvents such as decane or heptane, and most likely their mixture.

As for the spectrum characteristic for the decomposition of the solid part of the coating deposited after evaporation of the liquid part of solvents, a comparison with the database is shown in Fig. 5. The most similar spectrum retained in the database belongs to the gas emitted during the pyrolytic decomposition of the silicone Q-gum, which may indicate a coating based on silicone preparations.

On the last drawing no. 6 is presented with the direct visualization of data collected by the FTIR spectrometer depending on the wave number and temperature. With such a 3D presentation you can see how the nature of infrared spectra changes in general with increasing temperature and subsequent decomposition processes.

Fig. 6 visualization of data collected by the FTIR spectrometer depending on the wave number and temperature in the range from 30°C to 850°C.
SUMMARY

Conducted tests using Thermal Analysis and Fourier's FTIR infrared spectrometry techniques in showed that the solvent-free coating layer of KTX 07 remains thermally stable up to about 380°C in the air. Above this temperature, a multi-stage decomposition of the deposited silicone-based solid coating occurs, disrupting its integrity as a polymeric structure.

In addition, it was found that when the KTX 07 liquid coating is heated at a rate of 10 K/min, its liquid solvent part evaporates to a temperature of approximately 200°C completely. The maximum evaporation efficiency of the solvent part of the KTX 07 liquid coating was recorded, under given conditions, at a temperature of about 140°C, while the maximum rate of decomposition of the deposited solid silicone coating was recorded at a temperature of about 535°C.