

# THERMOGRAVIMETRIC ANALYSIS OF COMPOSITE MATERIALS WITH RUBBER MATRIX AND ADDITIVES OF FA RESPECTIVELY PVC

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**Abstract:** As previously specified, thermogravimetric analysis is a technique for thermal analysis of a material by which the change in mass (i.e. mass loss) is measured with the increase in temperature. The analysis can be performed in air or in an inert atmosphere such as nitrogen, helium or argon (the purpose is to prevent oxidation side reactions). The analysis allows the continuous weighing of a sample up to the predetermined final temperature. Depending on the type of equipment, the maximum mass of a sample may differ.

**Keywords:** PVC, rubber, fly ash, composite materials, industrial waste

## 3. INTRODUCTION

In the present work, a TGA Q50 thermogravimeter will be used, equipped with a nitrogen cylinder, the maximum sample mass being 1g. Figure 1 shows the working principle of thermogravimetry [1, 2]. An overview of the TGA Q50 thermogravimeter is given in Figure 2 [3].

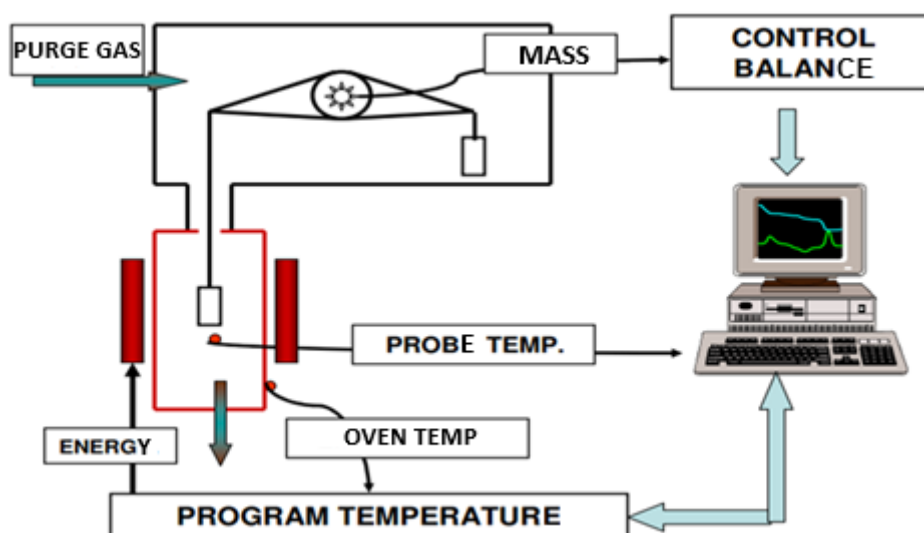


Figure 1. Working principle of thermogravimetry [2, 3]

The actual instrument that performs the thermogravimetric analysis consists of a microbalance (see Figure 3) that is surrounded by an electrically heated furnace, equipped with a thermocouple that constantly monitors the temperature during the actual experiment. The sample is placed on a crucible that is usually made of platinum and then placed in the oven. The microbalance, after scaling the crucible, measures the initial mass of the sample and then continuously measures its mass as the sample is heated to the chosen working temperature. During the experiment, the following curves are recorded, in real time, as the part heats up:

- loss of mass as a function of time (for isotherms);
- mass loss depending on temperature, if heating is carried out at a constant speed in °C/min.



Figure 2. TGA Q50 Thermogravimeter [3]

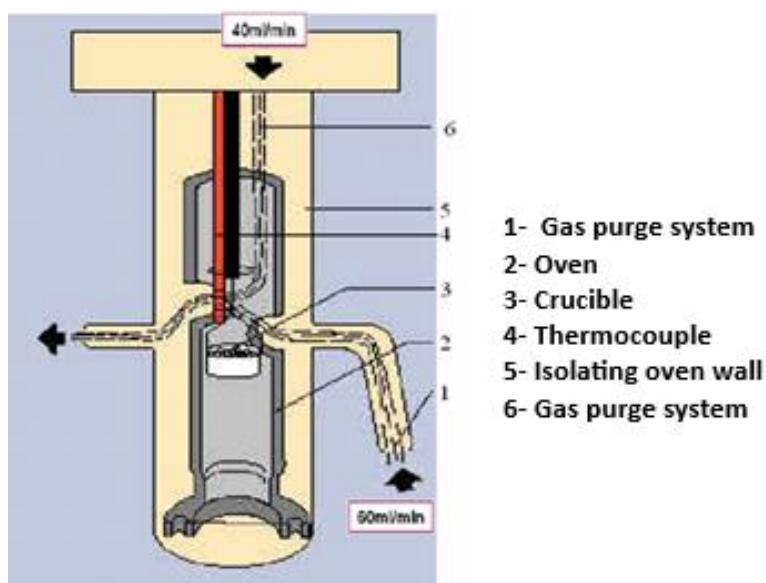


Figure 3. Microbalance Assembly [1]

Thermogravimetry provides particularly valuable information to assess material applicability, predict product performance and develop quality improvement strategies. This thermal analysis technique proves useful in the investigation of polymeric materials, including thermoplastics, heat resisters, and elastomers. It can also be successfully applied to complex materials such as composites, paints, coatings, films, fibers and curing agents.

The main applications of thermogravimetry are [1]:

- evaluation of the thermal stability of polymers;
- studying the resistance of polymers to oxidation;
- kinetic analysis of reactions in the presence of reactive gases (such as oxygen, air or other reactive gases) - for the purpose of studying pyrolysis, gasification and hydrogenation processes (useful in recycling methods);
- determination of residual solvent content;
- measurement of moisture content;
- determination of the content of inorganic curing agents introduced into polymeric materials or analysis of the composition of multicomponent systems;
- checking the purity of materials, whether organic or inorganic.

The component parts of the TGA Q50 thermogravimeter are given in Figure 4.

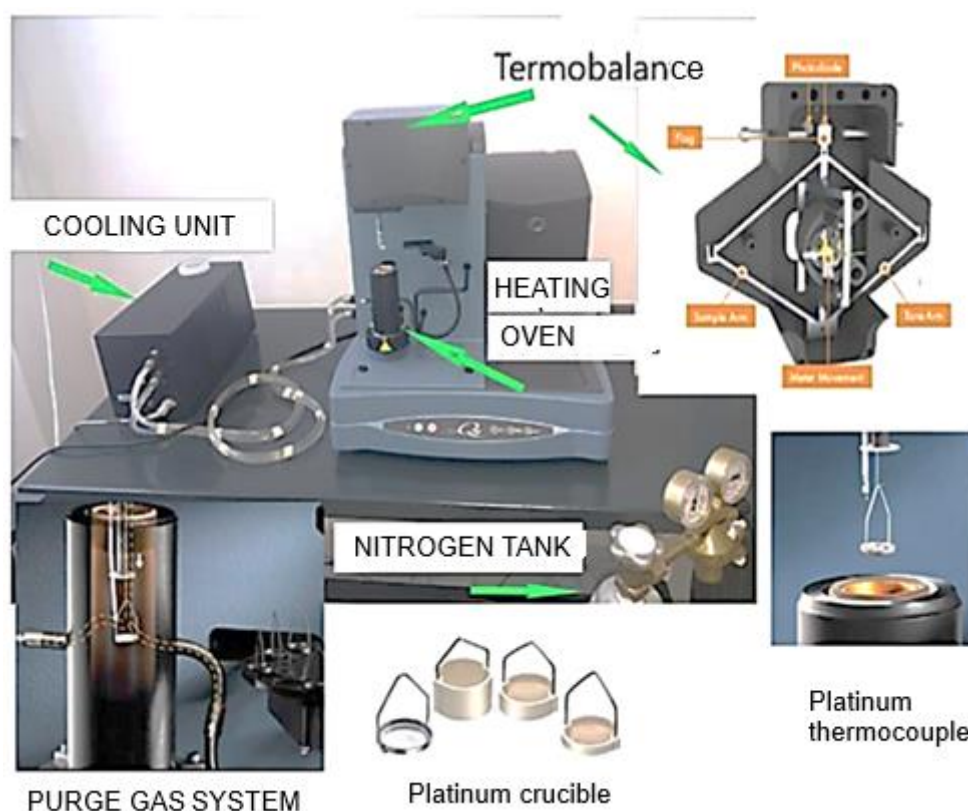


Figure 4. TGA Q50. Component element [4]

Analizele termogravimetrice au fost realizate conform standardului ASTM E1131-20 “Standard test method for compositional analysis by thermogravimetry” [5] dar și ASTM E 2550 “Standard test method for thermal stability by thermogravimetry” [6] .

The TGA Q50 used is supported by data acquisition software. It is accessed through the icon in Figure 5 and the menu in Figure 6 [7] appears.

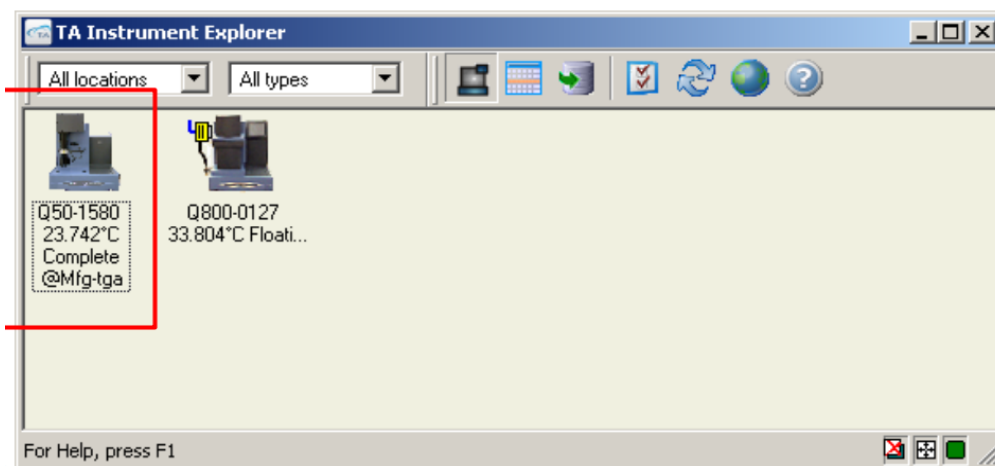


Figure 5. The icon for accessing the software [1, 7]

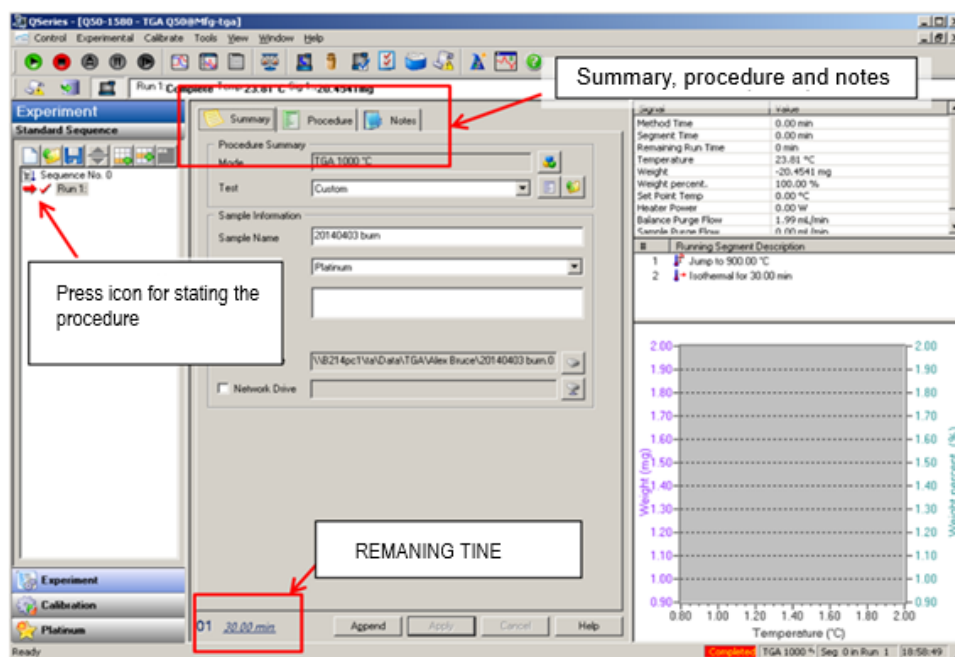


Figure 6. The icon for accessing the software [1, 7]

For the proper conduct of the experimental research, the following steps were taken:

- in the "Procedure" window, the type of test to be performed has been chosen, such as a ramp test, an isothermal test, a custom test, and others; if the custom test option is chosen, you can create your own process by clicking on the "Editor" option, which will open the segment editing screen;
- in the "Notes" tab, the name as operator or other characteristic data of the test performed has been entered;

- the icon for starting the experiment has been accessed; (Figure 6)
- a period of time has been waited until the sample will be heated to the chosen temperature, the remaining working time being indicated in the software (Figure 6);
- After the heating time is over, the experiment automatically stopped, the furnace lowered and the sample was removed from the crucible.

## 2. SAMPLE PREPARATION

For the analysis of the TGA, the following steps were taken:

- the crucible for each analysis has been loaded with a fraction of the specimen, with a mass below the maximum value indicated by the manufacturer (1 gram);
- a heating speed of 10<sup>0</sup>C/min has been chosen;
- the files with the analyzed samples were named one by one.

The program used was characterized by: Ramp method with a heating speed of 100C/min to 5000C in nitrogen environment (purity 6.0), then air cooling was done for 20 min.

The maximum heating temperature of 5000C was chosen because after this temperature the weight loss of rubber composites stabilizes. The working environment was made by means of a nitrogen cylinder connected to the device, and for all experiments the following were used:

- X comment Pan: Platinum;
- X comment Gas1: Nitrogen;
- X comment Gas2: Nitrogen;
- Xcomment Balance Gas: Nitrogen 40.0 ml/min;
- Xcomment Sample Gas: Nitrogen 60.0 ml/min;
- AirCoolTime 10.0 min.

## 3. EXPERIMENTAL DATA OBTAINED

Following the TGA analysis, 2 curves were drawn representing the mass loss of the sample (%) as a function of temperature (°C) and then the mass (%/°C) was derived as a function of temperature.

The TGA–DTGA results, using the high-resolution TGA approach, obtained from the 5 types of composite material (S01, S02, S03, S04, S05) are presented in Figures 7-11.

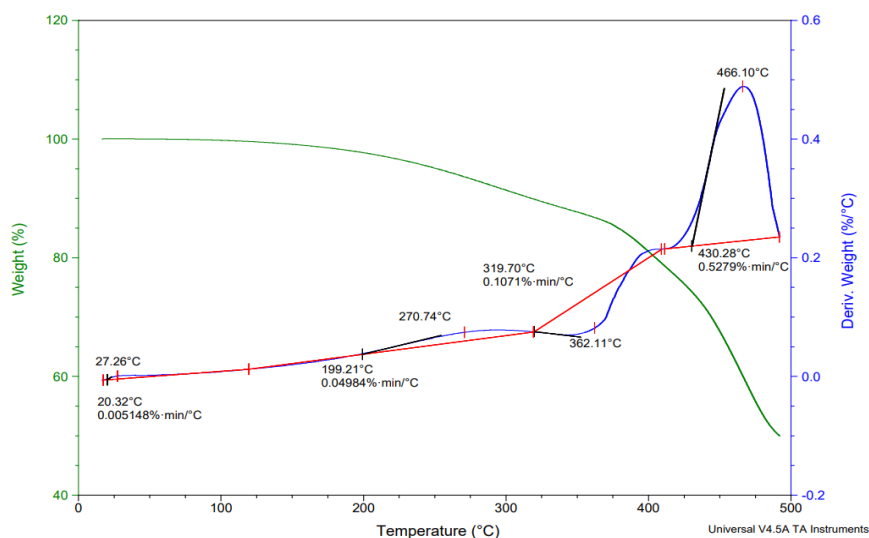


Figure 7. TGA Analysis for Specimen S01

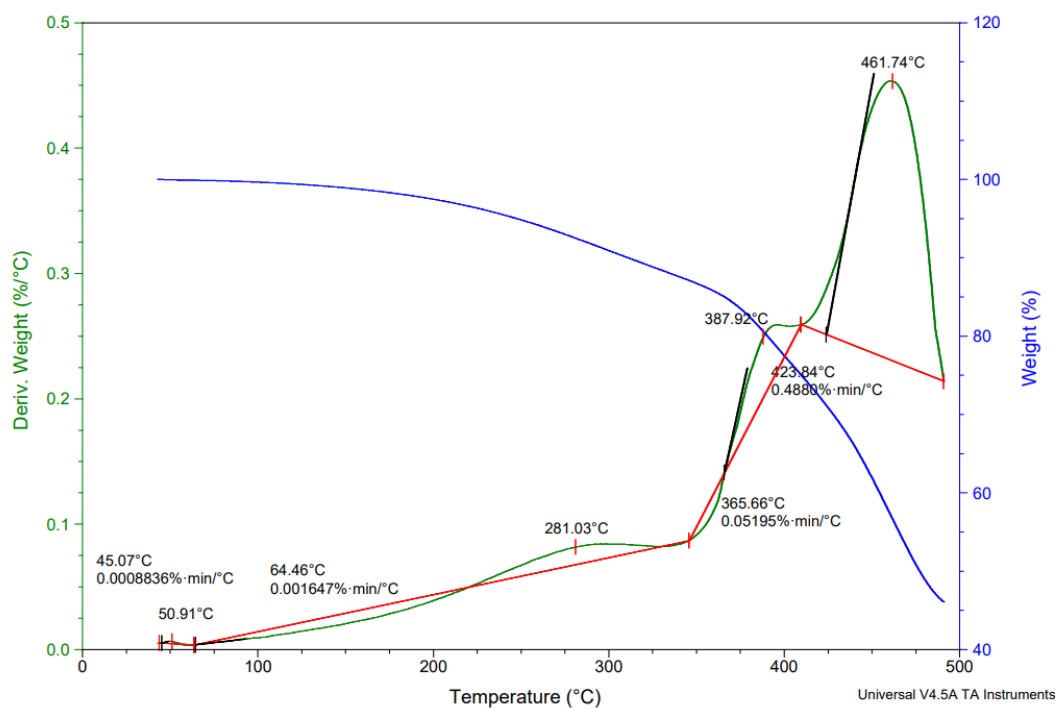


Figure 8. TGA Analysis for Specimen S02

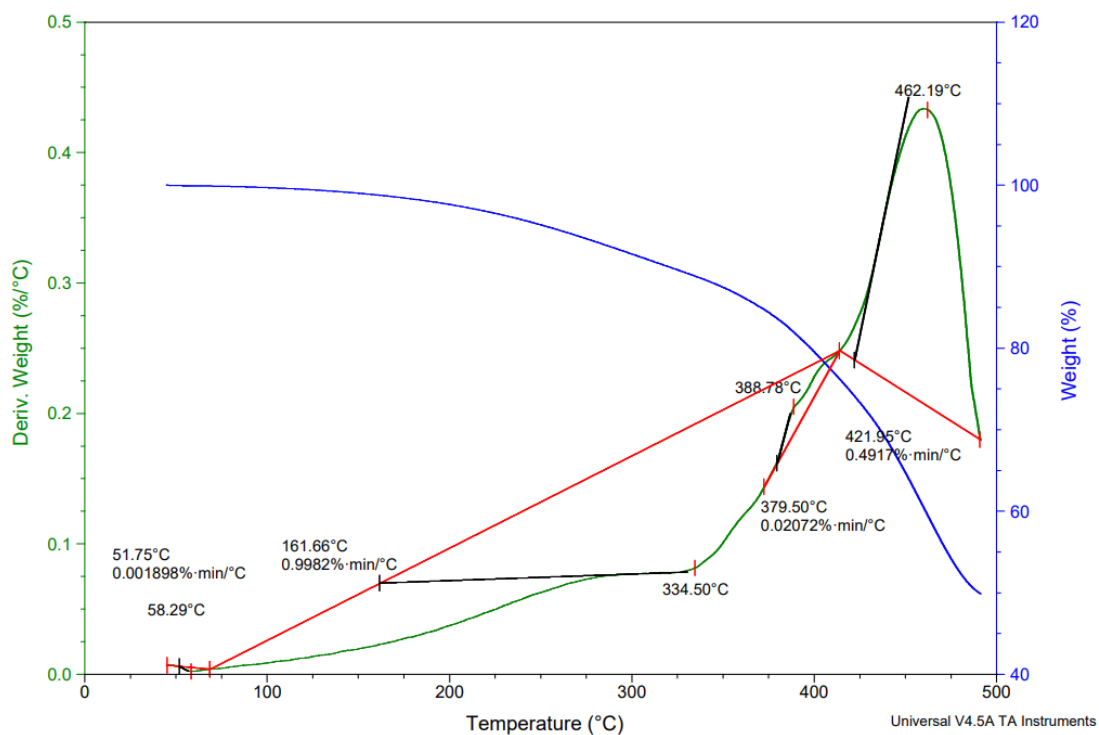


Figure 9. TGA Analysis for Specimen S03

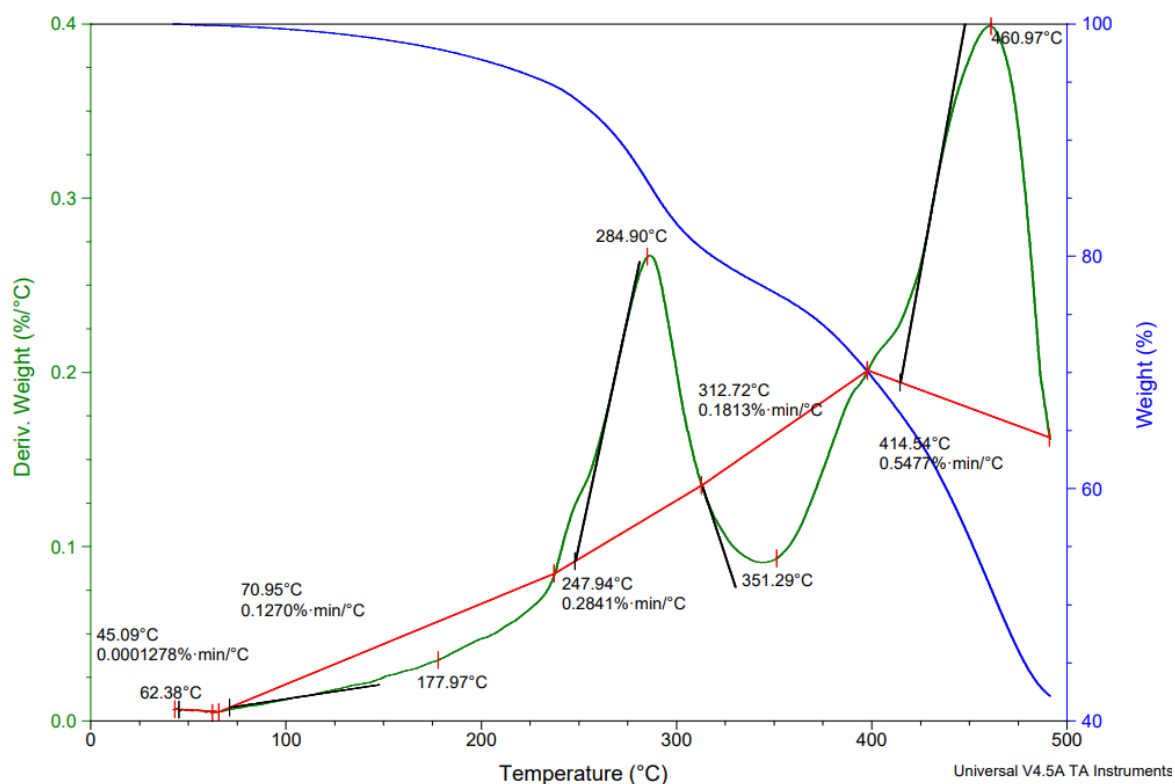


Figure 10. TGA Analysis for Specimen S04

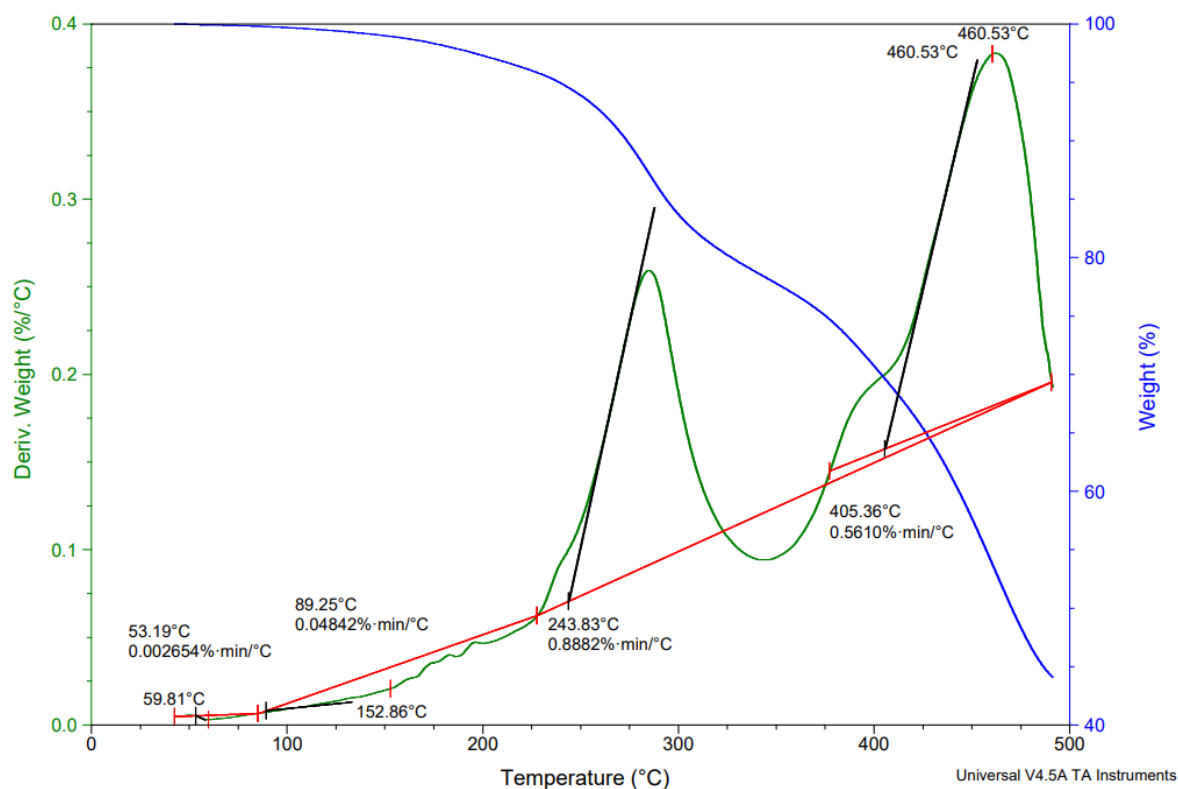


Figure 11. TGA Analysis for Specimen S05

From the analysis of Figures 7-11 it can be seen that the lowest mass loss was obtained for the S01 sample that does not have added residues (of AF or PVC). If AF is added to the rubber composition, there is an increase in both mass loss and loss rate. If a comparison is made between Figure 7 and Figure 8, it is found that the total mass loss was approximately 5% higher, reaching approximately 55% compared to the situation analyzed for the composite material that did not contain AF (S01). Also, the maximum mass loss rate was recorded at a temperature of 281.03°C, which is higher than the temperature of sample S01, but also at a temperature of 461.74°C, which is slightly lower than in the case of sample S01. As a general conclusion, if Figure 7 were to be compared with Figure 8, it can be said that there are no very large changes if AM particles are added to the rubber matrix. Somewhat it can be concluded that the AM residue retains, to a large extent, properties similar to the base material (rubber). For sample S03, from the analysis of Figure 9, it is found that the mass loss is similar to that of S01 (about 50%). The difference from S01 and S02 lies in the temperatures at which mass loss occurs at the highest speed. In the first stage, mass loss is observed at high speed, starting at a temperature of about 185°C (T0) and ending at 335°C. The second stage of high-speed degradation starts at about 335°C (T02) and ends at 462.19°C. A possible engineering explanation for the thermal degradation in this last stage is due to the fact that polyene sequences can occur in the structure of the composite material that produce volatile aromatic and aliphatic compounds through intramolecular cyclization of conjugate sequences. If PVC and FA residues appear simultaneously in the samples, then total mass periderite increases (maximum 55% for S05). It was found that for both S04 and S05 samples there are two temperature ranges in which mass loss occurs at a very high rate: 245°C - 285°C and 415°C - 460°C. As a general trend, it can be concluded that the thermal stability of specimens S04 and S05 decreases compared to the reference specimen S01.

#### 4. CONCLUSIONS

This method of analysis allows, in a shorter experimental time and with a high resolution, the analysis of the weight loss of composite materials at different temperatures. The TGA curve will usually indicate the breakdown of composite materials into their constituent components such as carbon black, regenerated rubber, filler, etc. as the temperature rises. TGA can also be used to determine the thermal stability of the composite material, the onset and peak temperatures of degradation, and the total weight loss of the material.

At the same time, the TGA also indicates the weight changes of FA, PVC as a function of temperature, and the TGA curve usually shows a gradual weight loss as the temperature increases, which is due to the thermal degradation of the organic compounds present in the structure of the material [8, 9, 10].

The TGA curve also helps to identify the temperatures at which specific compounds begin to degrade [11]. In the case of all 5 composite materials, weight loss occurs even at very low temperatures, and this weight loss is attributed to the volatilization of the processing oil or any other components with a low boiling point. As for the composite material S01 that does not have FA or PVC in its composition, it was observed that the total weight loss at 500°C was about 50%, and this corresponds to the rather high presence in the composition of inorganic filler components but also of rubber powder.

Since DTGA (Thermogravimetric Differential Analysis) curves can be used to identify and measure the proportion of elastomers in mixtures, the correlation between the height of the tips and the content of each component provides information about the rate of mass loss at different temperatures. From the analysis of the DTGA curve (Figure 5.6) it was observed that there is a high mass loss rate of 270.74°C, and this is due to the decomposition of natural rubber (NR), while the high rate of carbon loss with a DTGA peak at 466.1°C corresponds to the decomposition of styrene-butadiene rubber (SBR) and polybutadiene synthetic rubber (SKD ND), respectively. It is worth mentioning that at a temperature of 362.11°C it was observed that there is an area where the rate of mass loss decreases, and this may be due to the fact that the decomposition process of NR has ended, while the other components of the composite material have not decomposed.

As for the composite material containing FA (fly ash), following the TGA (Thermogravimetric Analysis) analysis, it was observed that the total mass loss was approximately 5% higher, reaching approximately 55% compared to the situation analyzed for the composite material that did not contain AF. Also, the maximum mass loss velocity was recorded at a temperature of 281.03°C, which is higher than the temperature of sample S01, but also at a temperature of 461.74°C, which is slightly lower than in the case of sample S01. Thus, it has been shown that the addition of AF in the rubber matrix composite material does not significantly change either the total weight loss or the temperatures at which weight loss occurs at the highest rate. This can be explained by the fact that the analyzed FA contains very fine fractions of ash or compound minerals (mainly silica) and thus a very good reaction with silanes (KWQ-EL) occurs. Also, the drop in temperature from 466.1°C to 461.74°C, at which the second stage of high-speed weight loss took place, can be explained by the presence of a certain fraction of AF with larger grains, which are not able to chemically react with silanes, and thus the temperature at which weight loss occurs changes.

In the case of composite materials (S03) where PVC is added in a moderate proportion, a total mass loss of approximately 50% has been observed, approximately the same as if PVC is not present in the composite material (S01). It is worth mentioning that in the case of the S03 test tube, the temperatures at which mass loss occurs at the highest speed change. It is worth noting that a first stage of high-speed weight loss starts at a temperature of about 185°C (T0) and ends at 335°C. The second stage of high-speed degradation starts at about 335°C (T02) and ends at 462.19°C. The thermal degradation in this last stage is due to the fact that polyene sequences can occur in the structure of the composite material that produce volatile aromatic and aliphatic compounds through intramolecular cyclization of conjugate sequences.

After the analysis of the S01, S02 and S03 composite materials, the next step was the TGA analysis of the composites containing both FA and PVC at the same time. Thus, S04 contains FA (30phr) and PVC (30phr), and in the case of the S05 composite material, the proportion of FA and PVC has increased considerably, reaching 50phr. It is worth mentioning that in the case of both composite materials (S04, S05), the total mass loss exceeds 55%, with a slight increase in the case of sample S05, which contains higher amounts of AM and PVC, respectively. Also, from the DTGA analysis it was observed that there are two temperature ranges in which mass loss occurs at a very high rate, namely the first temperature range (245°C - 285°C) and the second temperature range in which a very rapid mass loss occurred (415°C - 460°C). At the same time, it has also been confirmed that the presence of the coupling agent KWQ-EL can have a certain affinity for PVC, which can lead to an increase in the loss rate, especially in the temperature range 245°C - 285°C.

It is also worth mentioning that with the increase in the amount of AF and PVC, the total weight loss decreases from 58% to 55%. Thus, from the analysis of the TGA/DTGA curves, it can be confirmed that the thermal stability of the S04 and S05 composites decreases compared to the S01 sample, which does not contain FA or PVC in its composition. All these results can be attributed to the interaction between AM and PVC. This interaction can also be explained by the lack of a connection between the fillers and the rubber matrix.

The researches carried out with the objective of obtaining composite materials with high properties made from rubber waste, AM and PVC have demonstrated the following:

- it is possible to obtain composite materials from waste that have high performance in operation provided that their composition is optimized;
- the TGA/DTGA analysis has shown that the addition of AM and PVC causes a change in the mass loss values, but also in the temperature range in which this loss occurs;
- The mass losses are not very high, which means that this type of composite materials can be used in many different industrial applications.

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