

Study of Selected Composites Copper Concentrate-Plastic Waste Using Thermal Analysis

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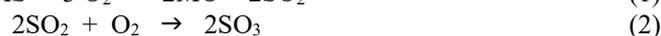
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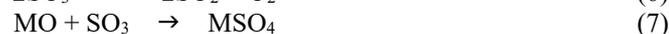
Abstract. The paper presents thermal analysis of selected composites (copper concentrate, plastic waste) in two stages. The first stage consisted in thermogravimetric analysis and differential thermal analysis on the applied plastic waste and copper concentrate, and subsequently, a comparative study has been carried out on products obtained, constituting composites of those materials. As a result of analyses, it was found that up to ca. 400 °C composites show high thermal stability, whereas above that temperature, a thermal decomposition of the composite occurs, resulting in emissions of organic compounds, i.e. hydrocarbon compounds and organic oxygenate derivatives.

1. Introduction

In metallurgic processes, thermal analysis allows to assess phase transitions of material decomposition. Each sulphide mineral has its specific oxidation temperature. The technology of metallurgic processing of sulphide minerals consists in a transition from sulphide to oxide. The degree of transition is characterized by sulphur content in the remaining material. Oxidation of bivalent metal sulphides follows the oxidation theory [1,2] (1-3):



According to the sulphate theory, oxidation of sulphides occurs in the following manner (4-7):



Production processes of lead, zinc, and copper from sulphide ores may be controlled at every specific temperature. Evaluation of each stage of production of transition and final products may be verified using DTA and TGA thermal analysis methods [2].



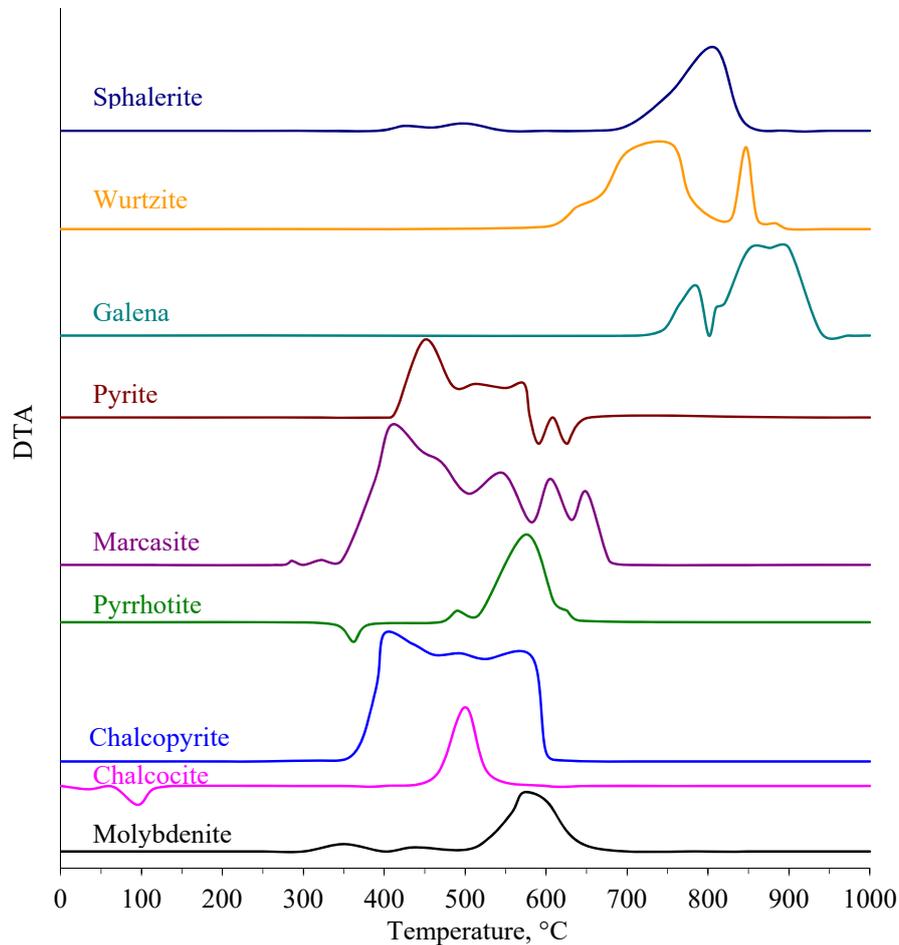


Figure 1. DTA curves of sulphide minerals [3]

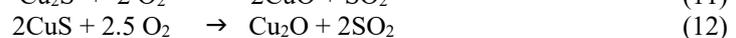
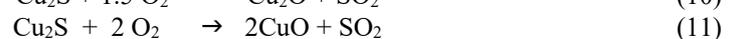
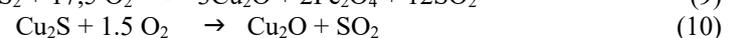
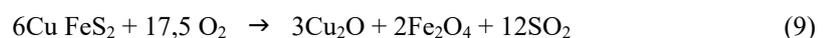
In the figure 1, the DTA curve shows oxidation of chalcopyrite during roasting. The process starts at 350-400 °C, and at 450 °C, it becomes intensified, which is reflected in a large, broad peak.

During heating of chalcopyrite in an inert atmosphere, dissociation occurs at 550 °C, in accordance with the following reaction (8):



Copper concentrate contains copper sulphides in the form of chalcocite (Cu_2S) and covellite (CuS) occurring with chalcopyrite. The DTA curve for chalcocite (figure 1) shows a small endothermic peak at 100 °C, responsible for phase transitions. The oxidation process in chalcocite occurs at 520 °C and is represented by a large exothermic peak [1,2].

Oxidation of copper sulphide minerals takes place at roasting temperature and follows the below mentioned reaction (9-12):



Copper and iron sulphides occur also in the form of intermediates. Oxidizing roasting of copper concentrate is conducted in max. temperature of ca. 900 °C, at which copper and iron sulphates dissociate, producing corresponding oxides.

2. Experimental

2.1. Materials and methods of examination

Thermal analysis consisted of two stages; the first stage consisted in a thermogravimetric analysis and thermal differential analysis for waste material applied and for copper concentrate; the second stage consisted in comparative study of obtained products constituting composites of those materials.

2.2. Measurement results

2.2.1. Thermal analysis of plastic waste

Recorded TG and DTA curves for plastic waste within the temperature range from 20 to 1000 °C are shown in figures 2 and 3. Weight losses up to 1000 °C are similar for all the studied materials determined based on the TG analysis and reach ca. 100 % by mass.

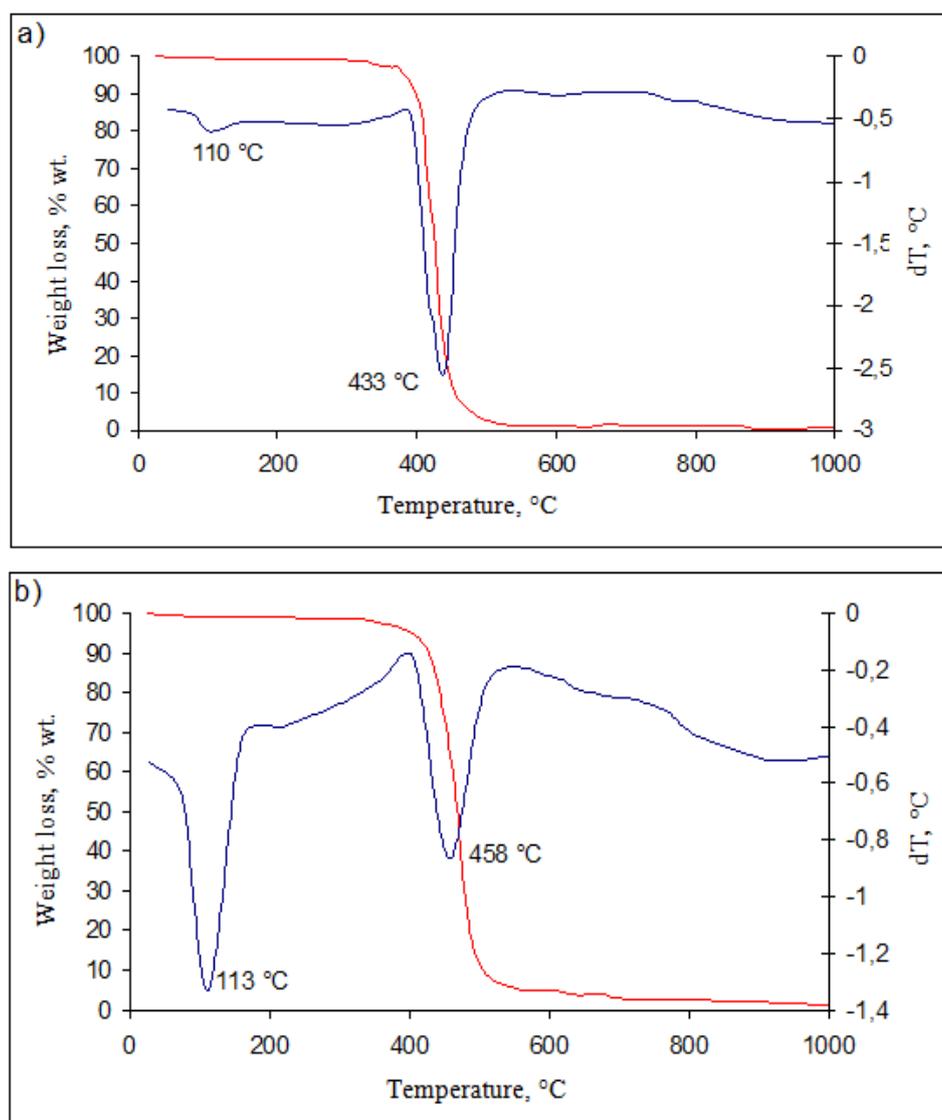


Figure 2. DTA curve (blue line) and TG curve (red line): a) waste PS, b) waste PP

DTA curves for plastic waste (PS, PE, PP) show a clearly visible peak at 110 - 114 °C, which signifies a phase transition of materials from glass to viscoelastic state and subsequent melting of the crystalline phase. In the case of polyethylene terephthalate (PET), the peak is shifted towards lower temperatures (92 °C). Polyethylene terephthalate is an amorphous polymer; therefore the melting effect of the crystalline phase is only residual. Those results are confirmed by studies of dynamic mechanical properties published in authors' previous papers [4,5,6,7]. DTA curves within the temperature range of 433-496 °C show an endothermic peak. At this temperature, total decomposition of the plastic occurs, reflected in the TG analysis (figures 2 and 3).

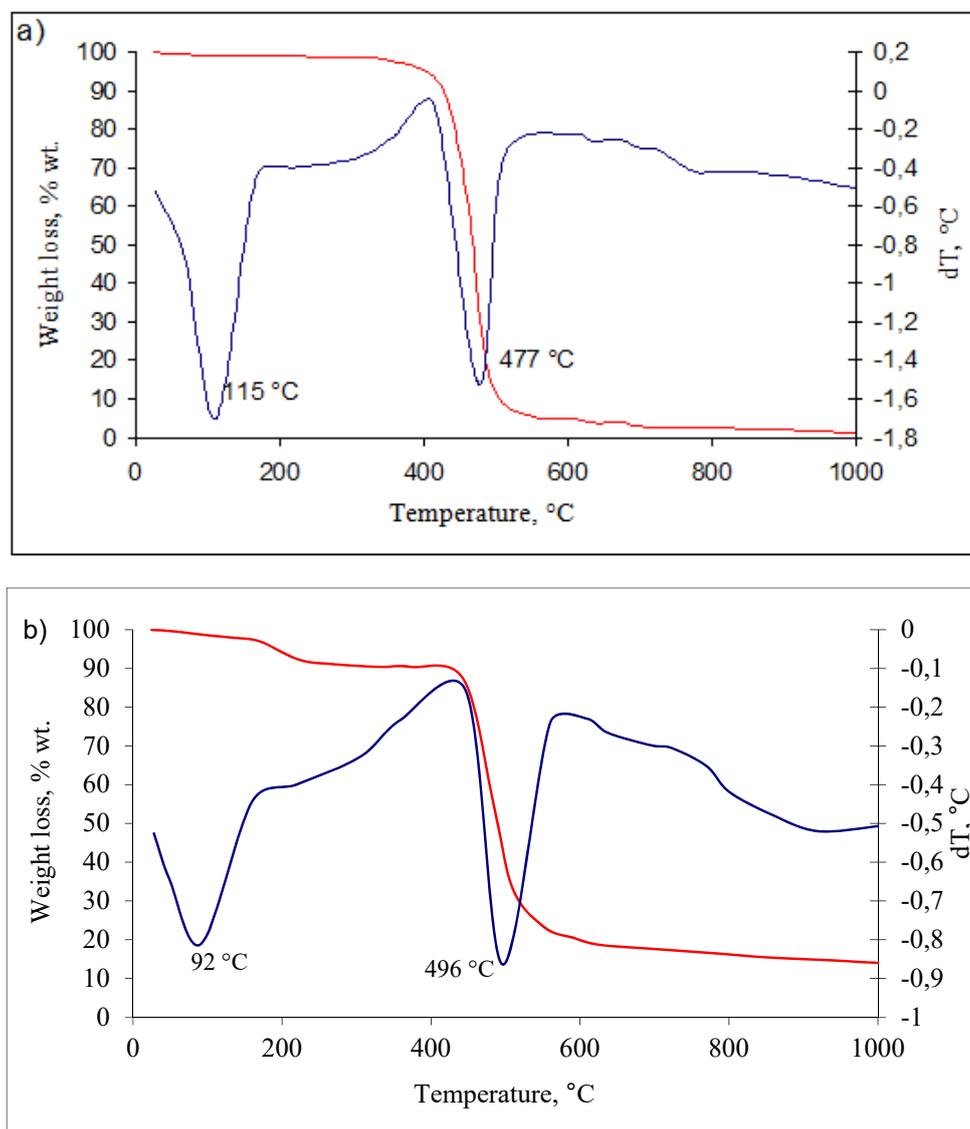


Figure 3. DTA curve (blue line) and TG curve (red line):
a) waste PE, b) waste PET

2.2.2. Thermal analysis of copper concentrate

Thermogravimetric analysis of copper concentrate (figure 4) has shown that, during decomposition, endothermic reactions occur, with total of approx. 19 %. At 164 °C, a peak occurs, corresponding to release of the physically adsorbed water, for which the weight loss is marginal - around 1.7%. In higher temperature ranges, a presence of two endothermic peaks with decomposition maxima at 502 °C and 778 °C was observed. In the first temperature range, decomposition of the organic

substance of copper concentrate occurs in ca. 3 % by mass, whereas in the second one – the inorganic substance decomposition occurs in ca. 15 %.

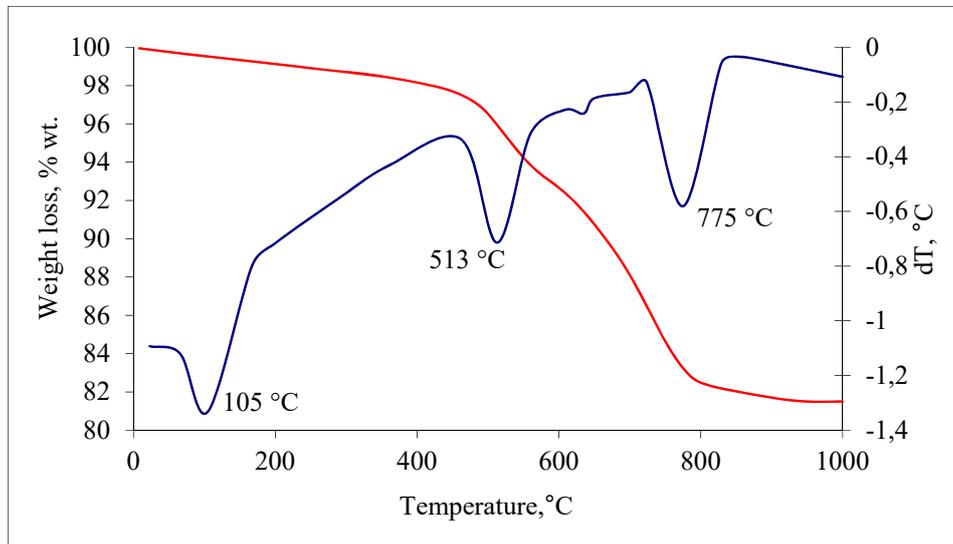


Figure 4. DTA curve (blue line) and TG curve (red line) for copper concentrate

2.2.3. Thermal analysis of composites of selected plastic materials (copper concentrate – plastic)

An analysis of thermal decomposition of composites (copper concentrate – polymer) was presented in figure 5 - 7. Composites formed at 180 °C were selected for thermal tests, containing the lowest studied binder content, i.e. 10 %. Thermal analysis of studied composites has shown that during heating up to 1000 °C, in the obtained moulders, endothermic reactions occur.

For a composite containing 10 % of PS by mass, the TG curve shows a weight loss starting at approx. 330 °C; the maximum of sample decomposition occurs at 427 °C. The decomposition of the plastic ends at 500 °C. Above 700 °C, inorganic substance decomposition occurs (figure 5). Total weight loss is 18 % by mass.

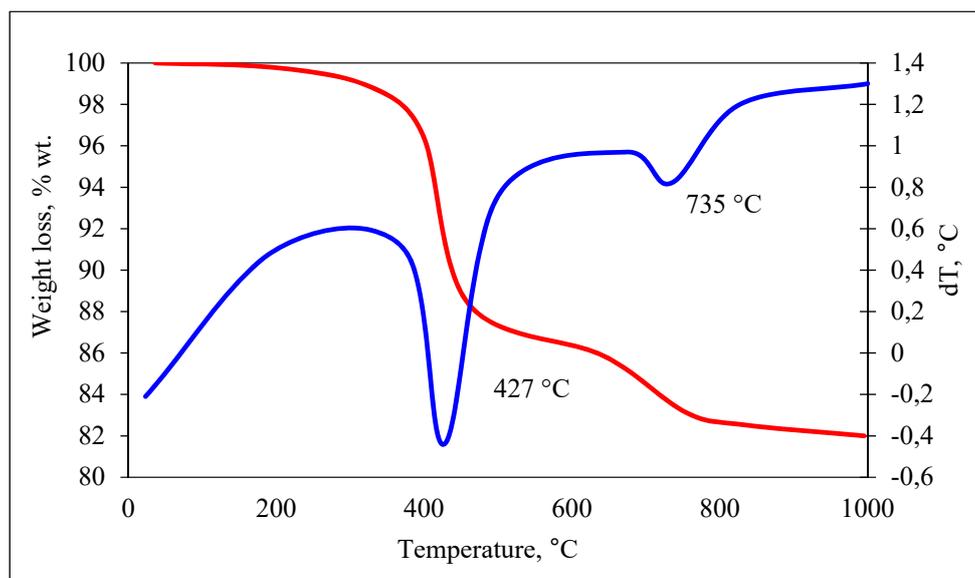


Figure 5. DTA curve (blue line) and TG curve (red line) of the PS 10 % composite

For the PE 10 % composite, formed at 180 °C, three endothermic peaks were observed. The TG curve of weight loss shows 27 % total weight loss (figure 6), starting at approx. 162 °C, and subsequent melting of the crystalline phase of the polymer. The starting point of the decomposition effect of the organic substance of the binder is at 450 °C, and the maximum of that decomposition is at 472 and 477 °C. At 772 °C, the DTA curve shows a pronounced endothermic effect, corresponding to the weight loss (TG curve). In that temperature, inorganic substance contained in the composite is decomposed (figure 6).

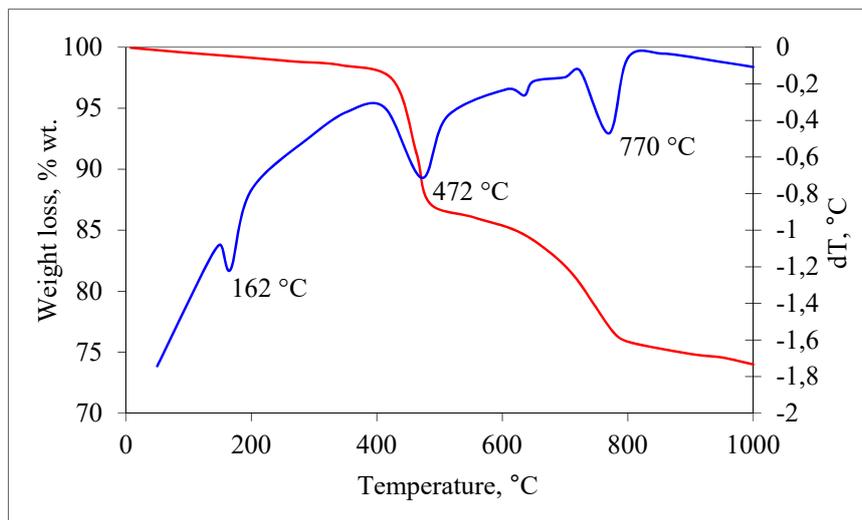


Figure 6. DTA curve (blue line) and TG curve (red line) of the PE 10 % composite

For the PP 10 % composite, similarly to the PE 10 % composite, three endothermic peaks were observed. Total weight loss was 26 % (figure 7). The starting point of the endothermic effect is situated at a comparable temperature, i.e. 164 °C, at which melting of the crystalline phase of the polymer also occurred. The decomposition of the binder organic substance starts at 420 °C; the decomposition maximum is at 472 and 635 °C. Inorganic substance decomposition of the sample occurs above 770 °C, which is comparable to the temperature of decomposition of inorganic substance in the case of PE 10 % composite (figure 6).

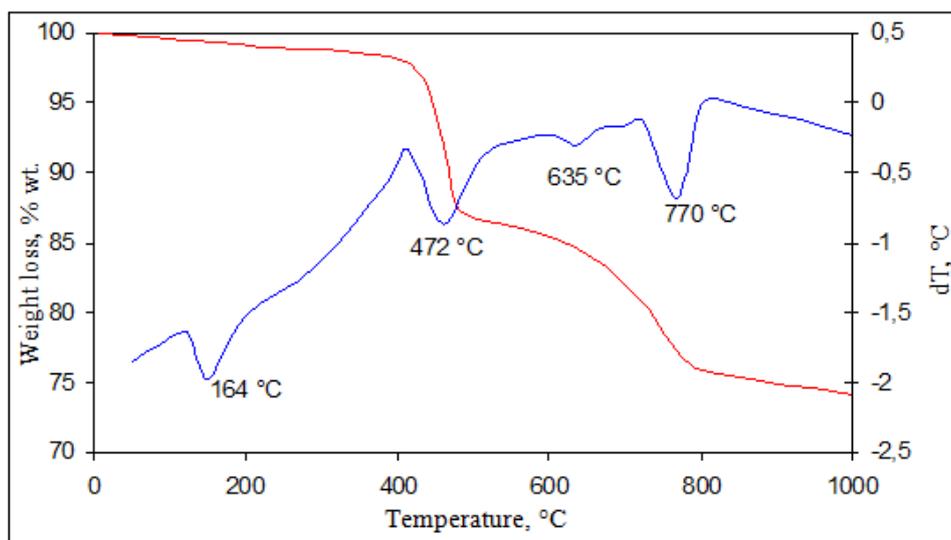


Figure 7. DTA curve (blue line) and TG curve (red line) of the PP 10% composite

2.2.4. Thermal analysis of the composite: copper concentrate – mixtures of plastic waste

Results of thermal analysis of a composite containing 10 % of binder by mass, i.e. PE/PP mixture with PE:PP weight ratios of 1:1, 1:2 and 2:1, were presented in figures 8-10. Results of the thermogravimetric analysis indicate that, regardless of the content of specific plastics in the composite, the entire weight loss is approx. 30 % by mass. Thermal analysis of the discussed composite has shown that during the decomposition, endothermic reactions occur. In the first temperature range, i.e. 160-165 °C, a peak occurs, corresponding to the melting of the crystalline phase in the studied polymers, for which the weight loss is marginal – around 1.5 %. In higher temperature ranges, two endothermic peaks were observed, with decomposition maxima at 469-473 °C and 771-782 °C. In the first temperature range, decomposition of the organic substance in the copper concentrate, and full decomposition of the binder occurs, in the quantity, as proven by a thermal analysis of plastic waste, of approx. 13 % by mass. In the other temperature range, the inorganic substance decomposition in the copper concentrate occurs, in a quantity comparable to three studied binders in the composites, i.e. approx. 13% by mass [4,5].

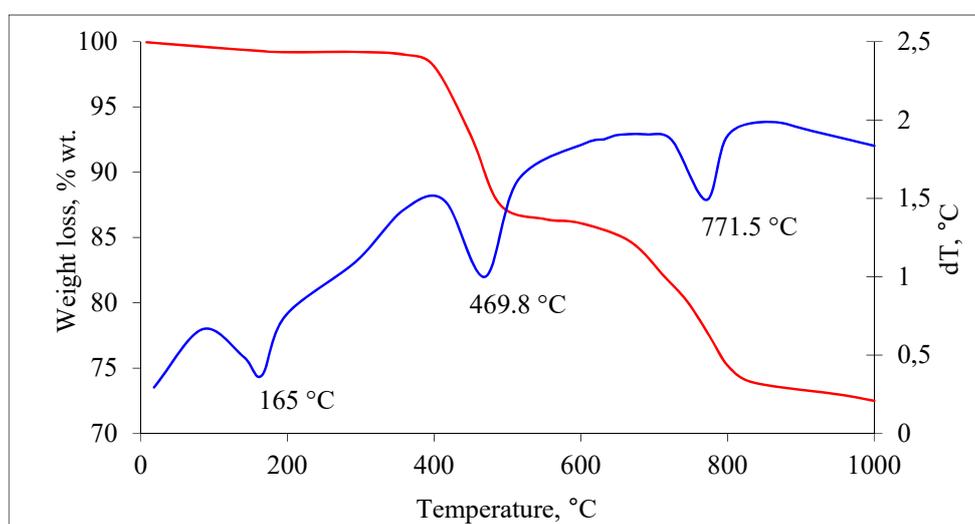


Figure 8. DTA curve (blue line) and TG curve (red line) of the PE/PP composite (1:1), with 10 % of binder content

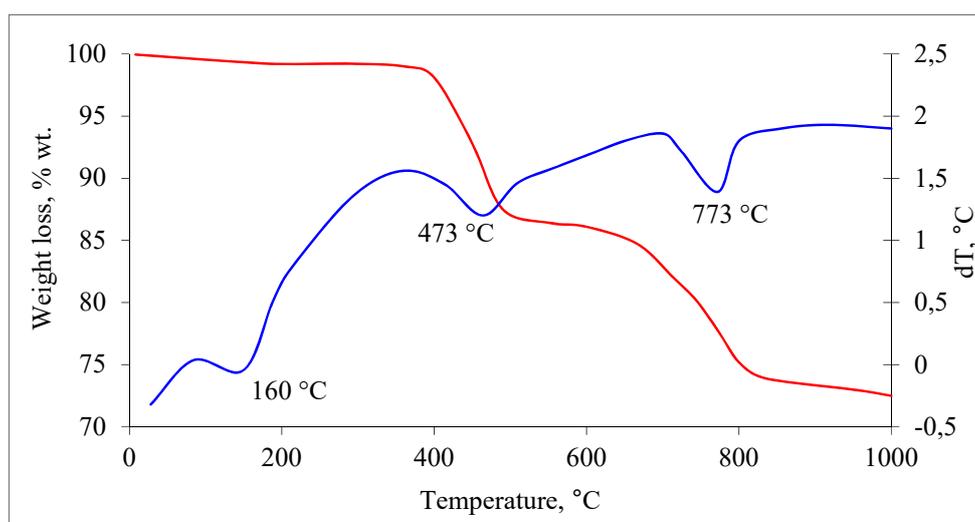


Figure 9. DTA curve (blue line) and TG curve (red line) of the PE/PP composite (2:1), with 10 % of binder content

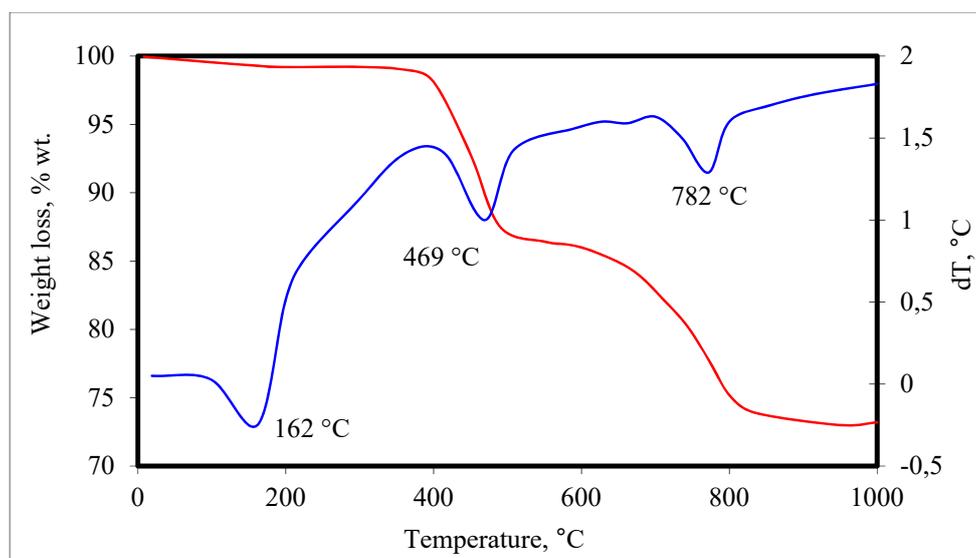


Figure 10. DTA curve (blue line) and TG curve (red line) of the PE/PP composite (1:2), with 10 % of binder content

3. Conclusions

1. Thermogravimetric analysis of the pure copper concentrate has shown that, during decomposition, endothermic reactions occur with total weight loss of ca. 19 %. At 164 °C, a peak occurs, corresponding to release of physically adsorbed water, for which the weight loss is marginal, i.e. approximately 1.7%.
2. DTA curves of analyzed plastics (PS, PE, PP) show a pronounced peak at a temperature range of 110 - 114 °C, which signifies a phase transition from glass to viscoelastic state, and melting of the crystalline phase.
3. Results of thermal analysis of the composite containing 10% of binder by mass, which was a mixture of PE/PP with PE:PP weight ratio of 1:1, 1:2 and 2:1, show that, regardless of different content of specific plastics in the composite, the total weight loss is ca. 30% by mass.
4. Above 400 °C, thermal decomposition of the composite occurs; as a result, organic compounds of the hydrocarbon type and derivatives of organic oxygenates are released.
5. Up to approx. 400 °C, composites show a high thermal stability.

Acknowledgment(s)

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