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# THE CHARACTERIZATION OF POLYMER COMPOSITES BY THERMOGRAVIMETRY

## TERMOGRAVIMETRIČNA KARAKTERIZACIJA POLIMERNIH KOMPOZITOV

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The characterization of polymer composites by thermogravimetric analysis was reviewed. The thermogravimetry of polymer composites was discussed with regard to the applied analytical conditions (heating rate, nature and flow rate of the carrier gas, mass and morphology of the sample). The influence of various types of fillers was analysed by discussing several examples such as PMMA/SiC, PS/SiC and PMMA/HAp composites.

Key words: polymer composites, thermogravimetry, effect of fillers, effect of analytical conditions

Pregled termogravimetrične karakterizacije kompozitov. TG se obravnava s stališča analitskih pogojev (hitrost segrevanja, narava in hitrost nosilnega plina, masa in morfologija vzorca). Vpliv različnih polnil je analiziran z obravnavo več vzorcev, npr. kompozitov PMMA/SiC, PS/SiC in PMMA/HAp.

Ključne besede: polimerni kompoziti, termogravimetrija, vpliv polnil, vpliv pogojev analize

## 1 INTRODUCTION

Thermogravimetry (TG) is a simple method of thermal analysis. In the International Conference of Thermal Analysis and Calorimetry (ICTAC) it is defined as a technique in which the mass of the sample is monitored against time or temperature, while the temperature of the sample, in a specified atmosphere, is programmed [1]. The technique was developed by scientists investigating various types of clay [2]. Although it is mostly used for standard measurements, such as the determination of moisture content and the amount of hydrated water in inorganic systems or for the assessment of volatiles content and the amount of inorganic filler in organic systems, the possibilities of thermogravimetry are much greater.

When determining the thermal stability of a compound or a composite material, the complexity of the interpretation of the results derived by thermogravimetry becomes apparent. The results depend on the applied heating rate, nature and flow rate of the carrier gas, the mass of the sample and to some extent also on its morphology. The results can be properly assessed only when additional information about the sample is available.

These problems become especially obvious when polymeric materials are characterized by thermogravimetry. Usually information on the thermal stability is sought and, to a lesser extent, information about material composition. It is also possible to calculate the thermal degradation activation energy on the basis of both isothermal and non-isothermal TG data by applying numerous methods available in the literature [3].

The majority of methods for calculating the activation energy of a sample based on non-isothermal TG data have limitations. Most of the methods yield results that are heating rate dependent and erroneous in regions where several degradation mechanisms overlap [4]. These difficulties have been overcome by modifications in the procedure, which include extrapolation to zero-heating rate [5] or separation of the thermolysis stages by peak splitting of the differential TG curves [6].

Some methods of activation energy determination, based on non-isothermal TG data, are better suited for certain types of polymers, based, for example, on whether or not they form char when heated. If the thermogravimetric data are based on isothermal measurements, the activation energy is determined in a straightforward fashion by applying the Arrhenius equation. Comparison of the values of the activation energy obtained by isothermal and non-isothermal TG data enables a selection of the optimal method for determining the activation energy of a particular polymer by a specific method based on non-isothermal TG data [7].

## 2 POLYMERIC MATERIALS

Non-conventional applications of thermogravimetry in the characterization of polymeric materials include the identification of specific functional groups based on their thermal stability, most commonly end groups [8]. It is also possible to differentiate polymers containing isomeric substituents, for example poly(di-n-propyl- and poly(di-iso-propyl itaconate) [9]. Information on how synthesis conditions can affect the polymer stability may also be obtained. Interesting examples are the thermal stability of polymethacrylonitrile synthesised in bulk or solution [10] or the stability of polymers obtained by the radical polymerization of methacrylates [11] or di-itaconates in the presence of chain-transfer agents, such as mercaptans [12].

Analysis of the thermal stability of polymeric materials becomes more complex when the polymers contain filler. The thermal stability of the polymer is affected by the nature of the filler (organic or inorganic), as well as its surface modification, morphology and size. The thermal stability of the material will increase as better polymer-filler interaction is achieved.

One of the ways to improve polymer-filler interaction is to optimize the mixing conditions and efficiently deagglomerize the filler. Filler deagglomerization is crucial in the preparation of nanocomposites, as it leads to changes in the material at a molecular level [13]. Such composites may be prepared by mixing polymer melt and nano-sized filler, by mixing polymer solution with the filler and evaporating the solvent under stirring and by “in situ” polymerization (or polycondensation) of monomer(s) with dispersed filler.

There are numerous papers in the literature dealing with nanocomposites based on silicate fillers – clays (a review is given in ref. [14]). For example, in the case of a composite based on clay and polyamide 6, the heat deflection temperature of the material under a load of 18.5 kg/cm$^2$ increases by 80 °C from 65 °C for pure polymer to 145 °C for a nanocomposite containing the mass fraction of clay 4.2 % [15].

Clay achieves better interaction with polar polymers. Thus composites of polystyrene and silicates do not have relevantly enhanced properties [16]. On the other hand, the composite of polystyrene and nano-sized CdS (up to 5 %, mean particle diameter 5 nm), prepared by evaporation from xylene solution, is markedly thermally more stable than pure polystyrene [17]. Composites of polystyrene with micro- [18] and nano-sized [19] $Fe_2O_3$ particles also exhibit considerably improved thermal stability of the material. Composites of "in situ" synthesised soy oil-based polyurethane with nano-sized $SiO_2$ particles are more thermally stable than the pure polymer [20].

## 3 POLY(METHYL METHACRYLATE)/SILICON CARBIDE COMPOSITES

The thermal stability and thermal degradation activation energy of poly(methyl methacrylate)/silicon carbide (PMMA/SiC) composites were investigated by non-oxidative non-isothermal thermogravimetry [21]. The size of the SiC particles ranged from 20 nm to 500 nm. PMMA was chosen as a convenient model system for the polymer component due to its fairly simple thermal degradation mechanism: depolymerization [11]. Consequently, the effects of SiC particles on the thermal stability of the composite may be easily noticed.

The α-SiC samples were commercial samples, while the β-SiC samples were laboratory synthesized [22]. The properties of the SiC particles are presented in **Table 1**. The amount of SiC in the samples ranged from 5 % to 50 % in order to show the effects of agglomeration. The composite samples were prepared by dispersing SiC particles in PMMA ($M_{w,o} = 1.25 \cdot 10^5$ g/mol) dissolved in dichloromethane and then evaporating the solvent under stirring.

**Table 1:** SiC powder properties
**Tabela 1:** Lastnosti prahov SiC

| Sample | Crystal modification | Particle diameter $d$/nm | Particle specific surface area $s$/(m$^2$/g) |
|---|---|---|---|
| SiC-nano | β | 20 | 75 |
| SiC-25 | α | 76 | 25 |
| SiC-15 | α | 127 | 15 |
| SiC-10 | α | 190 | 10 |
| SiC-9 | β | 500 | 9 |

The TG curves of pure PMMA, PMMA composite with the mass fraction of SiC-10 50 % and composite PMMA with 50 % of SiC-nano at various heating rates are shown in **Figures 1-3**. The TG curves of the other composites are similar. The TG curves are parallel and their shape does not depend on the heating rate. At 500 °C the polymer was completely decomposed. The SiC samples are stable in this temperature interval. The thermal stability of the composite increases with decreasing SiC particle size, **Figure 4**. The slopes of the TG curves of the composites change compared to the TG curve of pure PMMA. This change in slope is probably caused by the desorption of polymer or thermolysis volatiles from the SiC particle surface. As the particle

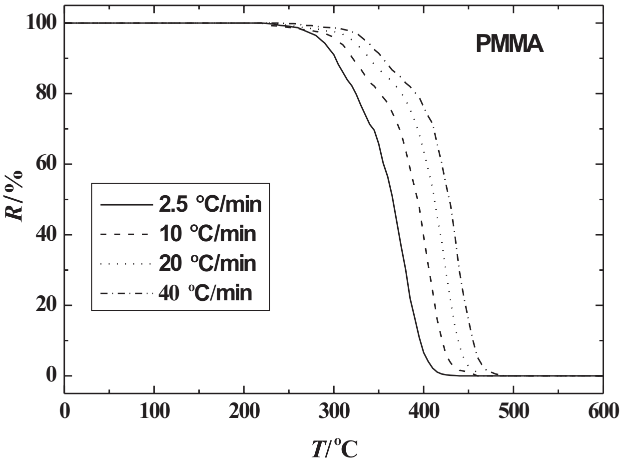

**Figure 1:** TG curves of PMMA, nitrogen flow rate 25 cm$^3$/min
**Slika 1:** TG-krivulje za PMMA, pretok dušika 25 cm$^3$/min

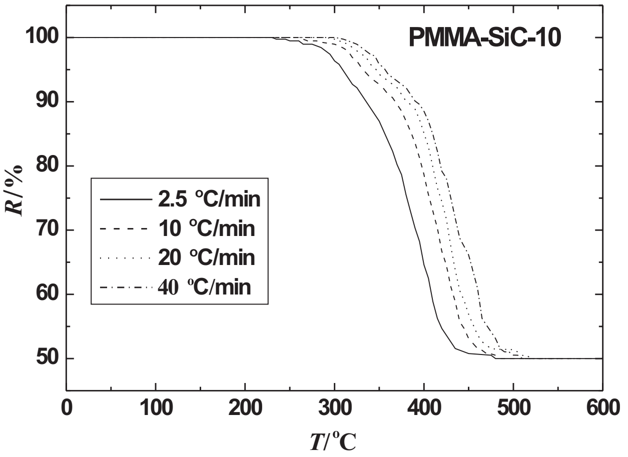

**Figure 2:** TG curves of a PMMA composite with the mass fraction of SiC-10 50 %, nitrogen flow rate 25 cm$^3$/min

**Slika 2:** TG-krivulje za PMMA kompozit z masnim deležem SiC-10 50 %, pretok dušika 25 cm$^3$/min

size diminishes, i.e. as the specific surface area increases, the mass loss is shifted toward higher temperatures, which is most clearly seen in the case of composite PMMA/SiC-nano. The composite thermal stability also increases with increasing amount of SiC, **Figure 5**. Although these results show that the presence of both micro- and nano-sized SiC increase the thermal stability of the composite, they give no information on the extent of polymer-filler interaction.

The thermal degradation activation energies, $E_a$, of the polymer and the composites were determined according to the Flynn-Wall method [23]. The values of $E_a$ of PMMA composites with 50 % of SiC particles of various diameters are presented in **Figure 6** as a function of mass loss (normalized to the organic part), while the mean values of $E_a$ are presented in **Table 2**. These results could indicate the degree of deagglomeration of SiC particles in the polymer matrix. In the case of PMMA composites with SiC-nano, $d$ = 20 nm, and SiC-25, $d$ = 76 nm, there is probably insufficient particle deagglomeration, hence the values of $E_a$ for these two samples do not differ significantly from those for the $E_a$ of pure

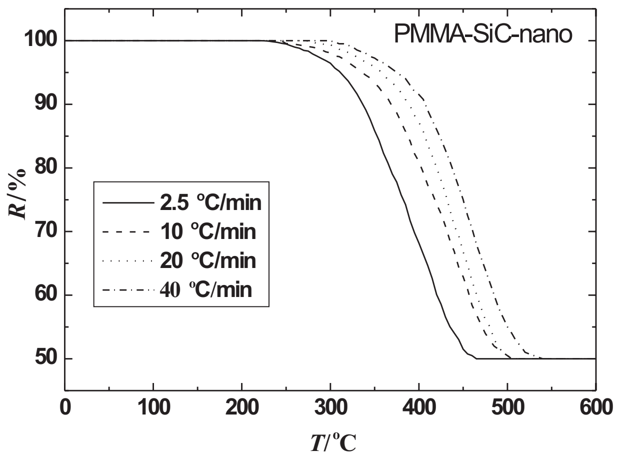

**Figure 3:** TG curves of a PMMA composite with the mass fraction of SiC-nano 50 mass %, nitrogen flow rate 25 cm$^3$/min

**Slika 3:** TG-krivulje za PMMA kompozit z masnim deležem SiC-nano 50 mas %, pretok dušika 25 cm$^3$/min

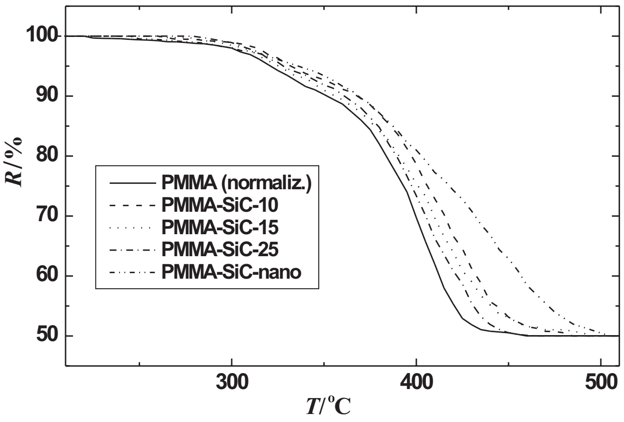

**Figure 4:** TG curves of PMMA and composites with the mass fraction of SiC-10, SiC-15, SiC-25 and SiC-nano 50 %, heating rate 10 °C/min, nitrogen flowrate 25 cm$^3$/min

**Slika 4:** TG-krivulje za PMMA in za kompozite z masnim deležem SiC-10, SiC-15, SiC-25 in SiC-nano50 %, hitrost segrevanja 10 °C/min, pretok dušika 25 cm$^3$/min

**Table 2:** Mean values of the thermal degradation activation energies of PMMA and PMMA/SiC composites ($w$(SiC) = 50 %)

**Tabela 2:** Povprečne vrednosti za aktivacijsko energijo termične degradacije PMMA in za PMMA/SiC kompozita ($w$(SiC) = 50 %)

| Sample | $E_a$ /(kJ/mol) |
|---|---|
| PMMA | 113.0 ± 14.2 |
| PMMA/SiC-nano | 113.9 ± 19.3 |
| PMMA/SiC-25 | 106.2 ± 23.3 |
| PMMA/SiC-15 | 125.2 ± 22.3 |
| PMMA/SiC-10 | 149.1 ± 20.4 |
| PMMA/SiC-9 | 154.8 ± 20.3 |

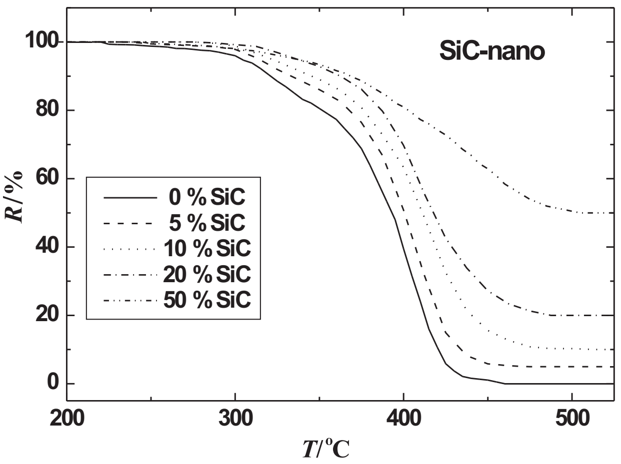

**Figure 5:** TG curves of PMMA and composites with the mass fractions of SiC-nano (5, 10, 20 and 50) %, heating rate 10 °C/min, nitrogen flow rate 25 cm$^3$/min

**Slika 5:** TG-krivulje za PMMA in za kompozite z masnim deležem SiC-nano (5, 10, 20 in 50) %, hitrost segrevanja 10 °C/min, pretok dušika 25 cm$^3$/min

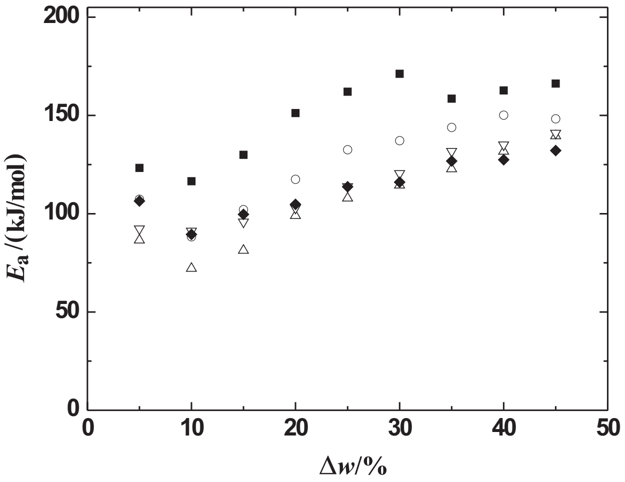

**Figure 6:** Dependence of the overall thermal degradation activation energy of PMMA (♦) and composites of PMMA with $w$ = 50 % SiC-10 (■), SiC-15 (o), SiC-25 (Δ) and SiC-nano (∇) on mass loss (normalized to 50 % mass loss)

**Slika 6:** Odvisnost splošne aktivacijske energije termične degradacije za PMMA (♦) in PMMA kompozite z $w$ = 50 % SiC-10 (■), SiC-15 (o), SiC-25 (Δ) in SiC-nano (∇) od izgube mase (normalizirano na 50 % izgube mase)

PMMA, although their specific surface areas are the highest. In the case of composites with larger particles, $d \geq 127$ nm, some particle deagglomeration occurs and there is a stronger polymer-filler interaction, even though the particle specific surface area is lower.

Similar behaviour was established when the influence of the amount of filler in the PMMA/SiC-nano was analysed in terms of the values of the $E_a$ (**Figure 7** and **Table 3**). When the SiC content was low, the values of $E_a$ of the composites were higher than in the case of the $E_a$ of pure PMMA. The SiC particles were deagglomerated and polymer-filler interaction was considerable. As the amount of filler increased, deagglomeration was not complete and the composite behaved as if the particles were of the micron range.

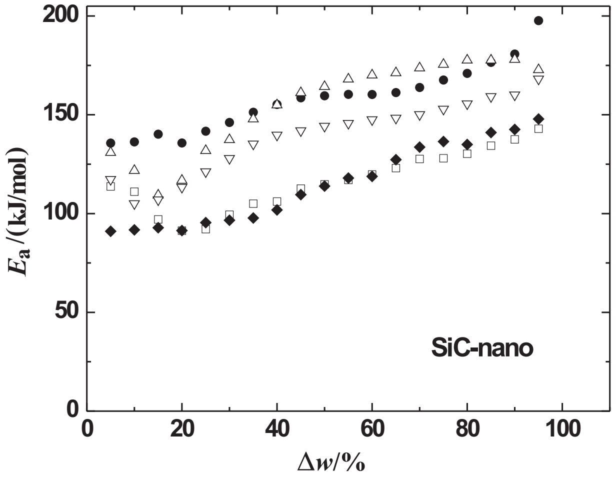

**Figure 7:** Dependence of the overall thermal degradation activation energy of PMMA (■) and composites of PMMA with $w$ = (5 (o), 10 (Δ), 20 (∇) and 50 (♦)) % SiC-nano on mass loss (normalized to 100% mass loss)

**Slika 7:** Odvisnost splošne aktivacijske energije termične degradacije za PMMA (■) in za kompozite z (5 (o), 10 (Δ), 20 (∇) i 50 (♦))% SiC-nano od izgube mase (normalizirano na 100 % izgube mase)

**Table 3:** Mean values of the thermal degradation activation energies of PMMA and PMMA/SiC-nano composites as a function of the amount of added SiC-nano

**Tabela 3:** Povprečne vrednosti za aktivacijsko energijo termične degradacije PMMA in za PMMA/SiC nanokompozite v odvisnosti od vsebnosti nanoprahu SiC

| Amount of SiC-nano ($w$/%) | $E_a$ /(kJ/mol) |
|---|---|
| 0 | 116.0 ± 15.2 |
| 5 | 157.9 ± 16.7 |
| 10 | 154.8 ± 23.0 |
| 20 | 139.0 ± 18.7 |
| 50 | 114.9 ± 20.1 |

If deagglomeration of the filler is more efficient, better polymer-filler interaction may be expected. When an ultrasonic probe was applied to deagglomerate nano-SiC dispersed in organic solvent, before proceeding to make the composite in the usual way, PMMA/SiC composites were obtained with distinctly higher thermal stability and higher $E_a$ values, even at high filler load (**Table 4**) [24].

**Table 4:** Mean values of the thermal degradation activation energies of PMMA and ultrasonically deagglomerated PMMA/SiC-nano composites as a function of the amount of added SiC-nano

**Tabela 4:** Povprečne vrednosti za aktivacijsko energijo termične degradacije za PMMA in za ultrazvočno dezagresiran PMMA/SiC nano kompozit v odvisnosti od vsebnosti nano prahu SiC

| Amount of SiC-nano ($w$/%) | $E_a$/(kJ/mol) |
|---|---|
| 0 | 116.0 ± 15.2 |
| 10 | 179.6 ± 13.0 |
| 60 | 133.8 ± 22.9 |

## 4 POLYSTYRENE/SILICON CARBIDE COMPOSITES

In order to confirm the applicability of this type of characterization, a series of SiC composites was prepared using polystyrene ($M_{w,0} = 8{,}58 \cdot 10^4$ g/mol) as the organic phase. Polystyrene has a more complex thermal degradation mechanism resulting in numerous thermolysis products of which monomer accounts for about 40 % of the volatiles [25]. Similar results were obtained as in the case of PMMA/SiC composites. SiC-nano was mechanically dispersed in styrene monomer and the composite was prepared by "in situ" radical polymerization [26]. The thermal stability of this composite and one with the same SiC concentration prepared from solution was compared and no significant differences were found (**Figure 8**). The activation energies of thermal degradation of PS/SiC composites with various SiC particle size are presented in **Table 5** [26].

**Table 5:** Mean values of the thermal degradation activation energies of PS and PS/SiC composites ($w$(SiC) = 50 %)
**Tabela 5:** Povprečne vrednosti za aktivacijsko energijo termične degradacije za PS in za PS/SiC kompozite ($w$(SiC) = 50 %)

| Sample | $E_a$/(kJ/mol) |
|---|---|
| PS | 116.0 ± 12.1 |
| PS/SiC-9 | 144.3 ± 5.2 |
| PS/SiC-10 | 122.1 ± 3.3 |
| PS/SiC-15 | 143.2 ± 11.3 |
| PS/SiC-25 | 141.4 ± 3.2 |
| PS/SiC-nano | 142.2 ± 12.3 |
| PS/SiC-nano-in situ | 147.1 ± 5.2 |

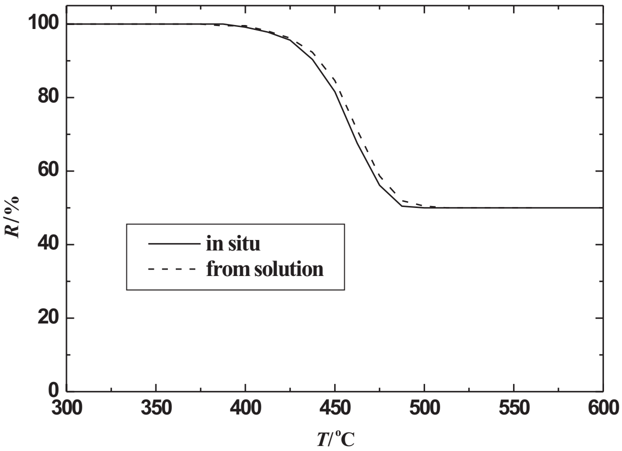

**Figure 8:** TG curves of PS/SiC-nano composites with the mass fraction of nano-SiC 50 % prepared by the "in situ" procedure and from solution, heating rate 10 °C/min; nitrogen flow rate 22 cm$^3$/min
**Slika 8:** TG-krivulje za PS/SiC-nano kompozite z masnim deležem nano-SiC 50 %, pripravljene z in situ postopkom iz raztopine, hitrost segrevanja 10 °C /min; pretok dušika 22 cm$^3$/min

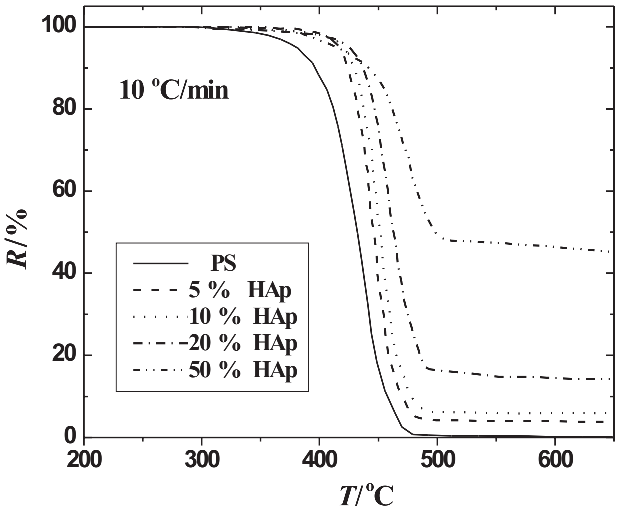

**Figure 9:** TG curves of PS and composites with the mass fractions of (5, 10, 20 and 50) mass % HAp, heating rate 10 °C /min, nitrogen flow rate 25 cm$^3$/min
**Slika 9:** TG-krivulje za PS kompozite z masnim deležem (5, 10, 20 in 50) % HAp, hitrost segrevanja 10 °C/min, pretok dušika 25 cm$^3$/min

## 5 POLYSTYRENE/HYDROXYAPATITE COMPOSITES

Polystyrene/hydroxyapatite (PS/HAp) samples were prepared from solution as in the previous cases adding various amounts of nano-sized HAp [27]. The mean diameter of the HAp particles was about 100 nm. The goal of this series of experiments was to show whether homogeneous composites could be obtained from solution, considering the difficulty of keeping HAp uniformly dispersed in the polymer solution. The TG curves of PS and PS/HAp composites are presented in **Figure 9**. The values of the thermal degradation activation energy of PS and the composites, **Table 6**, indicate that appropriate deagglomeration was obtained at low filler load.

**Table 6:** Mean values of the thermal degradation activation energies of PS and PS/HAp composites as a function of the amount of added HAp
**Tabela 6:** Povprečne vrednosti za aktivacijsko energijo termične degradacije za PS in PS/HAp kompozite v odvisnosti od vsebnosti dodanega HAp

| Sample | Mass loss range $\Delta w$/% | $E_a$ /(kJ/mol) |
|---|---|---|
| PS | 10–90 | 111.6 ± 12.9 |
| PS/HAp (5 % HAp) | 10–90 | 165.0 ± 3.8 |
| PS/HAp (10 % HAp) | 10–85 | 145.8 ± 3.2 |
| PS/HAp (20 % HAp) | 10–60 | 86.0 ± 2.8 |
| PS/HAp (50 % HAp) | 5–47.5 | 92.9 ± 3.0 |

## 6 CONCLUSIONS

The examples presented above illustrate some applications of thermogravimetry in the characterization of composites. Polymer-filler interaction may influence the values of the overall thermal degradation activation energy of the organic phase of the composite, thus indicating that a nanocomposite has been formed. The information provided by thermogravimetry can supplement information obtained by microscopy and investigations of mechanical properties.

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