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Highly sensitive TGA diagnosis of thermal behaviour of laser-deposited materials

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ABSTRACT

Thermal gravimetric analysis (TGA) combining the use of digital microbalances, gas-chromatography and mass spectroscopy is demonstrated as a highly sensitive technique for the determination of thermal behaviour of polymeric materials obtained in very low quantities in laser-induced chemical processes. The article is a brief review on some authors' TGA studies of materials prepared by laser ablation of polymers, laser-induced chemical vapour deposition and laser back-side etching in the gas phase. The TGA-diagnosed materials are (i) chemical vapour-deposited N-containing polyoxocarbosilane and Fe/polyoxocarbosilane composites, (ii) crosslinked polymers ablatively deposited from pure and metal particles-loaded poly(vinyl acetate), poly(vinyl chloride-co-vinyl acetate) (PVACVC) and poly[oxy(tetramethyldisilane-1,2-diyl)] (POTMD), and (iii) carbon/polyoxocarbosilane composites obtained through gas-phase etching process.

1. Introduction

Digital recording balances is a very sensitive instrument handling changes in masses of up to 150 and 450 mg with a sensitivity of 10^{-4} mg and respective accuracy of 5 and 10%. The instrument can be applied to studies of a variety of chemical and physical phenomena accompanied with mass changes as, e.g. adsorption, desorption, hydrogenation, dehydrogenation, hydration, dehydration, thermal decomposition and the like. Previously, we have studied the kinetics of adsorption of gaseous hydrocarbons, ammonia, methanol, water and pyridine on various catalysts as, e.g. γ-alumina and silica [1–5].

It is common knowledge that the digital recording balances can be used for examinations of thermal behaviour of various substances or their mixtures in flow as well as static systems at temperatures of up to 1200 °C and at atmospheric or lower pressures. Advantageously, it can be also applied in studies involving formation of aggressive gaseous products, in which cases the measuring component of the system must be protected in a flow of pure inert gas. Commercial digital recording balances are suited for studies of chemical phenomena with samples of commercial or easily lab-produced chemicals that weight several tens of milligrams [1–7]. In these cases, the measurements are highly reliable and fully guaranteed by the instrument producer.

Difficulties begin when samples to be studied are provided in low quantities and when increasing these quantities is a laborious task [8–11]. Such a problem is particularly widespread with materials prepared by laser-induced processes which yield only minute amounts of solid products, or they give rise to very light materials (ultrafine powders) which, fully packed into the balance container, correspond to weights lower than 1 mg. Despite these severe constraints, successful thermal gravimetric analysis (TGA) measurements are still possible provided that special measures are taken.

In this paper we report on our recent studies of thermal properties of novel, laser-deposited polymeric materials [6–18]. These materials were produced in the form of ultrafine (ultralight) powders and thin films as a consequence of laser-induced ablative, gas-phase chemical and gas-phase etching deposition. These materials possess unique structures suggesting their use in several applications, especially as thermally stable protective coatings and lubricants. The production of polymeric materials of demanded properties requires that the laser-induced chemical processes have to be performed at a variety of experimental conditions (irradiation parameters, precursor pressures) and that the materials obtained in each run must be examined. Typical laser-chemical deposition system works with several up to several tens of μmol of polymeric precursor and allows deposition of very low (normally 0.5 to few mg) quantities of the solid product. These amounts are sufficient for analyses by FTIR, Raman, NMR, X-ray-photoelectron (XP) and Auger spectroscopy and electron microscopy. Also thermal behaviour of mg or sub-mg quantities of these polymeric materials can be elegantly evaluated by the suitable digital recording balances coupled with another measuring device such as a gas chromatograph and a mass spectrometer. This set-up allows continual monitoring of gaseous (volatile) products of the decomposition and provides the explorer with both mass changes of the analyzed sam-

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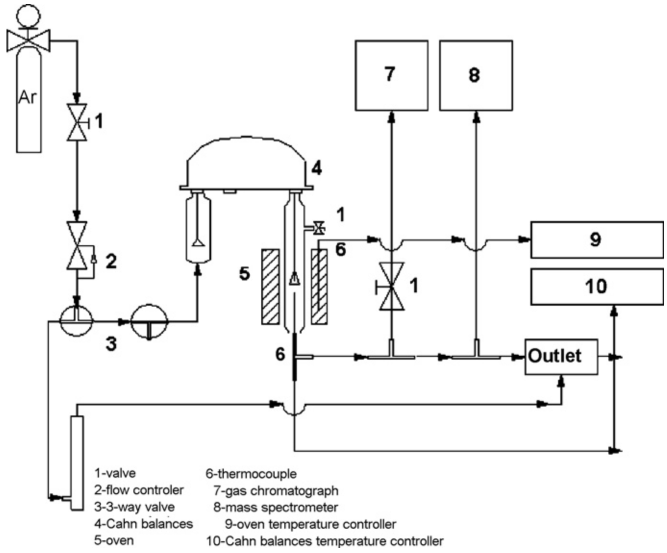

Fig. 1. A set-up used for TGA studies of laser-obtained samples.

ple and quality and quantity of the volatile products, giving thus adequate information on the course of the thermal degradation process. Complementary FTIR or Raman spectral analyses of the TGA residuum then allow getting a substantially complete view on the whole degradation process.

2. Experimental

Thermal stability of laser-obtained products provided in low quantities was examined in a set-up consisting of thermal gravimetry, gas-chromatography and mass-spectrometry (Fig. 1).

Typical thermal decomposition of the laser-obtained materials was conducted by heating the sub-mg or mg samples to 600 °C, (or 900 °C) at the rate of 4 °C/min, using a Cahn D-200 recording microbalances in a stream of inert gas (Ar, He) at the flow rate 100 ml/min. The sample was heated in the oven (Clasic Co.) output of which was regulated by a Clasic Clare 4.0 programmable digital temperature controller. The flow of carrier gas was controlled by electronic mass-flowmeters (306 KA/RA, Theiva Co. and AFC 2600 PRO Alborg Co. models). Alongside with the decrease of the sample weight, the composition of the outgoing gases was analyzed every 10 min by an automatic sampling gas chromatograph (a GC 5890 Hewlett-Packard instrument) with FID and TCD detectors and a 2 m long (i.d. 2 mm) Porapak P packed column. Simultaneously, the outgoing gas was repetitively analyzed on a mass spectrometer (a VG GAS Analysis LTD instrument) which run in a multiple ion monitoring mode (MIM, 16 specific ions selected) and allowed the data to be displayed and stored as a time-dependent plot. The data obtained from the gas chromatograph and the mass spectrometer were semi-quantitative due to very high dilution of the gaseous decomposition products (concentrations just above the detection limit).

For the very low-weight samples, the shape of the weight decrease vs. time curve is affected with changes in gas density, flow rate and diffusion of the volatilized sample (and the products of the sample decomposition) in the course of sample heating. These changes required that the experimental weight vs. time curves had to be specifically corrected. The same amount of the sample and an inert substance (e.g. glass) was measured at exactly the same conditions and the obtained TGA curves for each were added or subtracted (depending whether carrier gas flowed upwards or downwards the measuring tube). Another limitation was considered when thermal behaviour of a laser-deposited product and a structurally similar conventional material was to be compared. In these instances, TGA analyses of both samples must have had had similar volumes.

The samples for TGA were prepared by laser-induced processes when intense IR or UV laser radiations is absorbed in gaseous or solid polymer precursor and results in chemical processes that are part of laser ablation of polymers, laser-induced chemical vapour deposition and laser back-side etching in the gas phase. The laser-induced chemistry results in (i) the formation of reactive transient species that undergo polymerization and (ii) deposition of ultrafine solid particles (powders or non-adhering films). These materials were collected from the appropriate reactors as described in references given below.

3. Results and discussion

Several examples of highly sensitive TGA–GC–MS analyses applied to minute amounts of laser-deposited materials are given below and briefly discussed.

3.1. Thermal degradation of laser-deposited Si/O/C/N/H solid powder

Megawatt ArF laser photolysis of gaseous methyldisilazanes $[(CH_3)_nH_{3-n}Si]_2NH$ ($n = 2, 3$), namely tetramethyldisilazane (TMDSZ) and hexamethyldisilazane (HMDSZ) in excess of Ar allowed chemical vapour deposition of ultrafine Si/O/C/N/H solid powders with structure consistent with N-containing polyoxocarbosilane [14]. These powders contain Si-centred radicals and possess nanometer-sized texture and high specific area. The TGA of these materials was carried out with respective initial sample weight 1.7 and 3 mg, heating to 700 °C at the rate of 4 °C/min and carrier Ar gas. Fig. 2 shows an example of the raw (measured) data and the data corrected for changes in gas density, flow velocity and diffusion of the volatilized sample (decomposition products) during the heating.

The corrected thermograms of the powders (Fig. 3) show that the materials are quite stable and lose their weight by only several per cent. The GC analysis of the evolved gases allows explanation of the weight losses by assuming two responsible processes which are sublimation and decomposition to volatile hydrocarbons.

The minute weight losses during the heating were explained on the basis of FTIR and XP spectra of the TGA residua in terms of thermal reorganization of structures to solid oxycarbonitride described as a network of interconnected Si, C, O and N atoms.

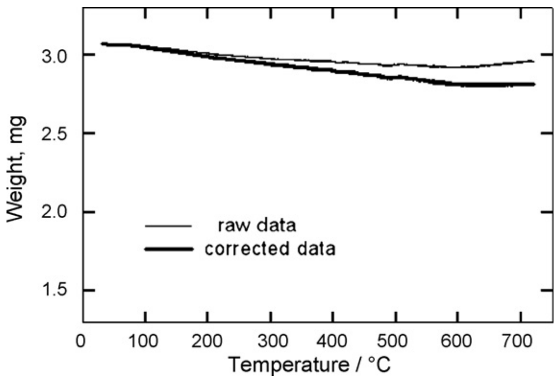

Fig. 2. The weight decrease vs. temperature for sample produced from HMDSZ with raw and corrected data.

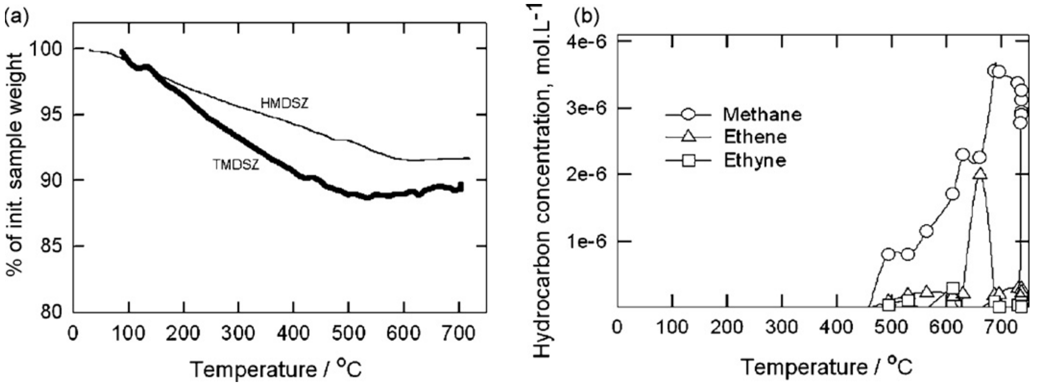

Fig. 3. Thermogram for the deposits from HMDSZ and TMDSZ using corrected data (a) and gases evolved during TGA of the deposit from HMDSZ (b).

3.2. *Thermal behaviour of polyoxocarbosilane in Fe-based (core)-polyoxocarbosilane (shell) nanocomposite*

IR laser-induced decomposition of iron pentacarbonyl in mixture with methoxytrimethylsilane affords chemical vapour deposition of nanocomposites composed of an iron-based core and polyoxocarbosilane shell [15]. Thermal decomposition of the polymer shell in the composites possessing different Fe content was carried out by heating the initial 6–20 mg samples to 700 °C at the rate of 4 °C/min in Ar carrier gas. It was revealed that the thermal degradation is a two-stage (low- and high-temperature) evolution of methane and that thermal stability of the nanocomposites is remarkably dependent on the Fe content (Fig. 4).

The observed gaseous decomposition products are methane, hydrogen, methylsilanes and carbon oxides (formed from the oxidized Fe surface). The two-stage degradation (Fig. 5) was considered as revealing two different mechanisms of polymer degradation. The low-temperature decomposition (facilitated at higher Fe content) occurs as a heterogeneous process on the Fe core and the high-temperature degradation takes place with the polymer not being in contact with Fe core.

3.3. *Thermal degradation of poly(vinyl acetate) and crosslinked laser-derived analogue*

IR laser-induced ablation of poly(vinylacetate) (PVAC) yields polymeric material containing conjugated C=C bonds and less acetoxy groups [7]. This material undergoes fast crosslinking at the C=C bonds upon staying. The polar conjugated “intermediate” and the final saturated crosslinked material represent novel polymeric systems and belong to family of polar polymers. They are of interest because of their potential as gel polyelectrolytes and protecting films.

The thermal stability of these polymers was examined with sample weights 4–16 mg, heating to 600 °C at the rate 4 °C/min in Ar carrier gas. It was demonstrated that thermal behaviour of the polymeric intermediate (deposit 1) and of the aged (crosslinked) polymer (deposit 2) differ from that of the parent PVAC. The comparison of the decomposition profiles is consistent with both materials losing less weight than the parent PVAC (Fig. 6). Furthermore, the crosslinked polymer loses less weight than does the freshly prepared conjugated intermediate, which indicates that the crosslinking leads to higher thermal stability.

3.4. *Thermal degradation of metal/poly(vinyl acetate) composites and laser-derived analogues*

Pulsed IR laser-induced ablation of PVAC loaded with nm-sized Cu and µm-sized Fe particles allows deposition of metal/polymer composites with polymeric component crosslinked and less polar [8]. Thermal degradation of these laser-deposited composites was performed with samples of 13–30 mg, heated to 700 °C at the rate of rate 4 °C/min in Ar carrier gas. The TGA of the parent metal/PVAC blends and of the deposited materials is compared in Figs. 7 and 8. It is seen that both thermograms display two-stage degradation processes which differ in the position of both stages: the PVAC decompositions peak at 310 and 420 °C, whereas that of the crosslinked products are centred at higher (360 and 460 °C) temperatures. It is demonstrated that thermal stability of the crosslinked

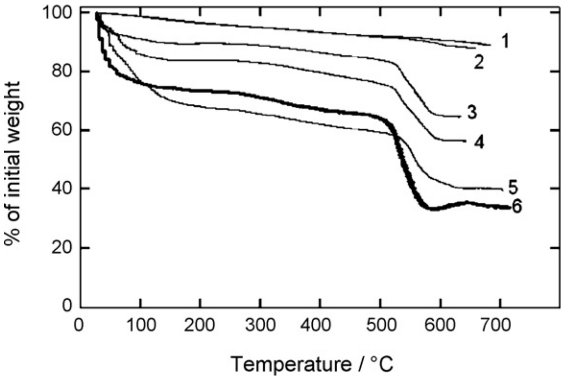

Fig. 4. Thermograms of Fe/polyoxocarbosilane nanocomposites having 32, 45, 63, 65, 73 and 76 wt% of Fe (corresponding curves 1–6).

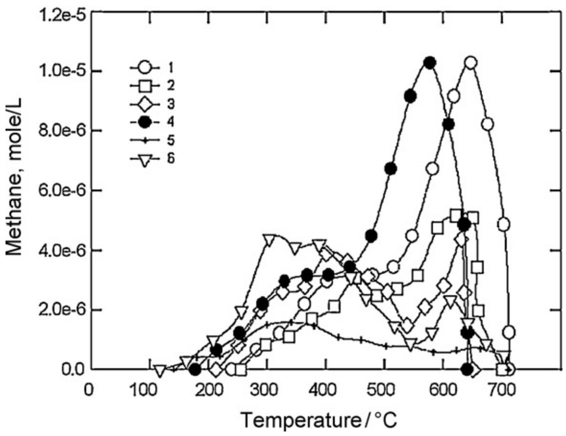

Fig. 5. Evolution of methane in thermal degradation of Fe/polyoxocarbosilane composite (designation 1–6 as in Fig. 4).

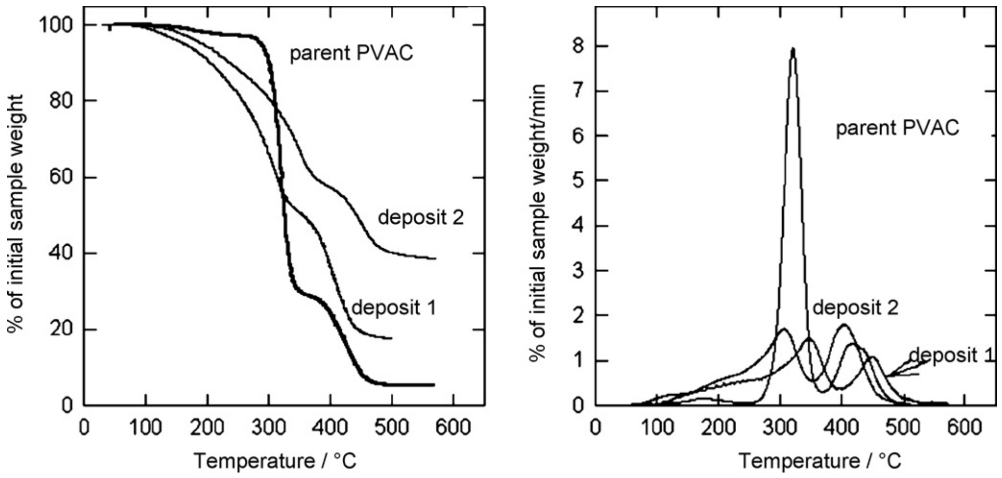

Fig. 6. Thermograms of the parent PVAC, the freshly prepared (conjugated) polymer (deposit 1) and the aged (crosslinked) polymer (deposit 2).

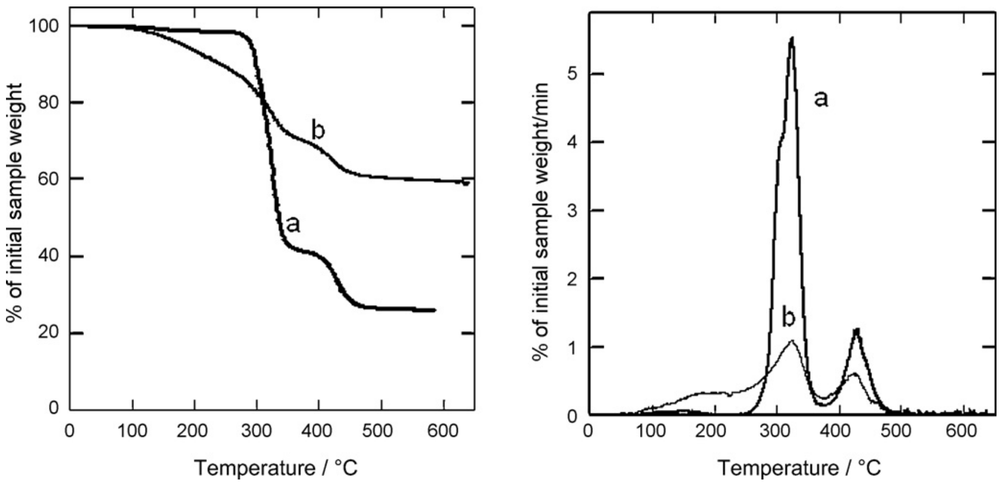

Fig. 7. Thermograms of parent PVAC/Cu composite (a) and laser-derived product (b).

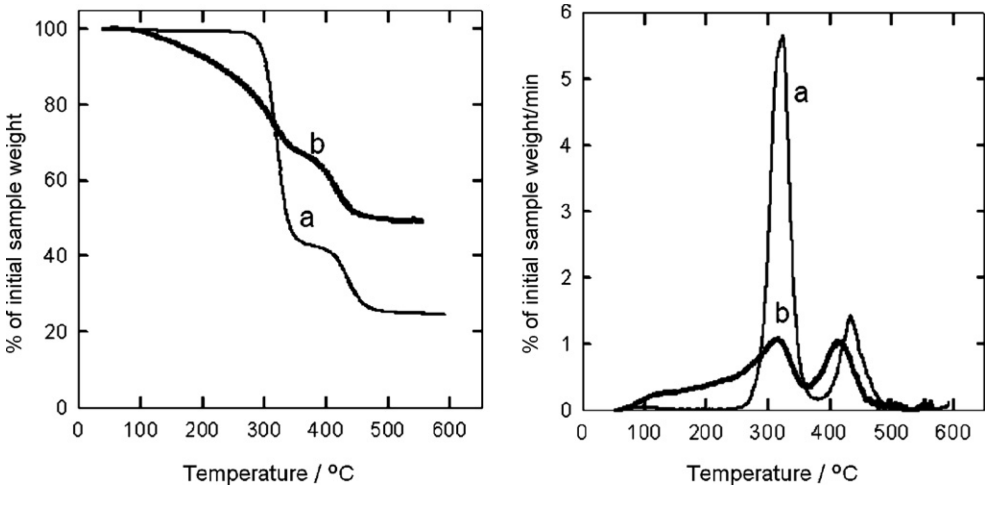

Fig. 8. Thermograms of parent PVAC/Fe composite (a) and laser-derived product (b).

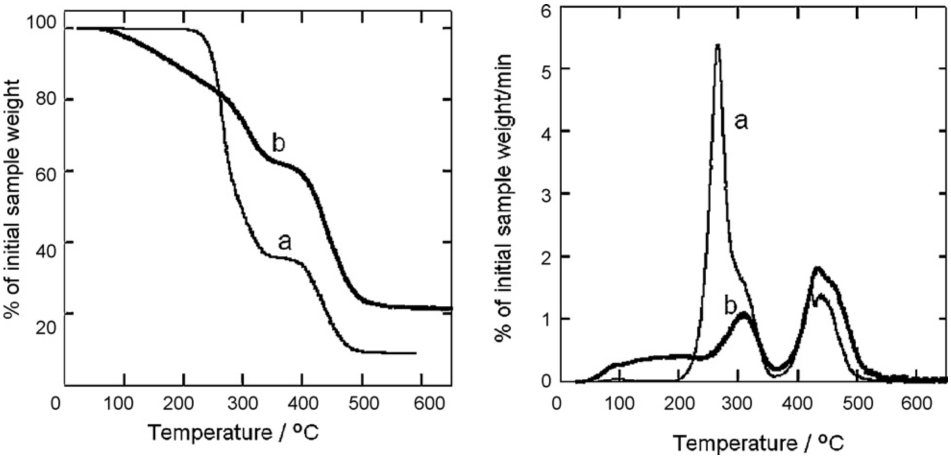

Fig. 9. Thermal decomposition and rate of thermal decomposition of poly(vinyl chloride-co-vinyl acetate) (a) and laser-derived analogue (b).

laser-derived polymer is decreased by incorporation of Fe microparticles or Cu nanoparticles.

3.5. *Thermal degradation of poly(vinyl chloride-co-vinyl acetate) (PVACVC) and its laser derived analogue*

Pulsed IR laser-induced ablation of poly(vinyl chloride-co-vinyl acetate) allows deposition of thin films of a crosslinked analogue that has lower content of the polar groups [6]. TGA of the parent polymer (commercial sample, 70 mg) and of the laser-derived polymer (15 mg) was carried out by heating the samples up to 700 °C at different heating rates and with Ar carrier gas.

The conventional degradation of PVACVC occurs through cleavage of both pendant groups; it yields acetic acid and HCl as major volatile products along with a non-polar carbonaceous residue. The thermograms of the parent PVACVC and of the laser-derived product (Fig. 9) reveal that thermal degradation of both samples is considerably different.

Several main products evolved from both samples upon heating were detected through their mass spectral fragmentation. The diagnostic single-ion traces at *m*/*z* 16, 28, 36, 43 and 44 are in the given order due to CH_4, CO, HCl, CH_3CO_2H and CO_2 (Fig. 10).

The major degradations differences relate to the decomposition progress, evolution of volatile products and the yield of the carbonaceous residue. More feasible cleavage of acetate- and Cl-pending groups and the higher yield of the carbonaceous residue being observed for the laser analogue were explained in terms of structural differences between the parent and laser-derived polymer. The more feasible elimination of the polar groups was ascribed to the accelerating effect of the neighbouring C=C bonds and the higher yield of the carbonaceous residue was attributed to the crosslinking.

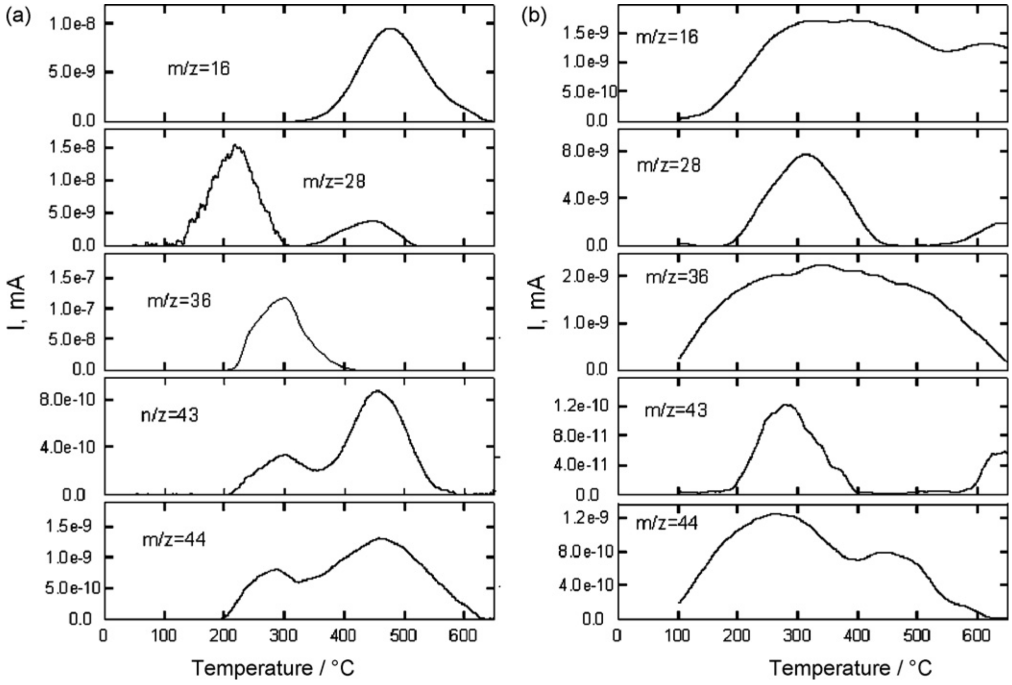

Fig. 10. Single-ion traces of the main products from TGA of PVACVC (a) and laser-derived product (b).

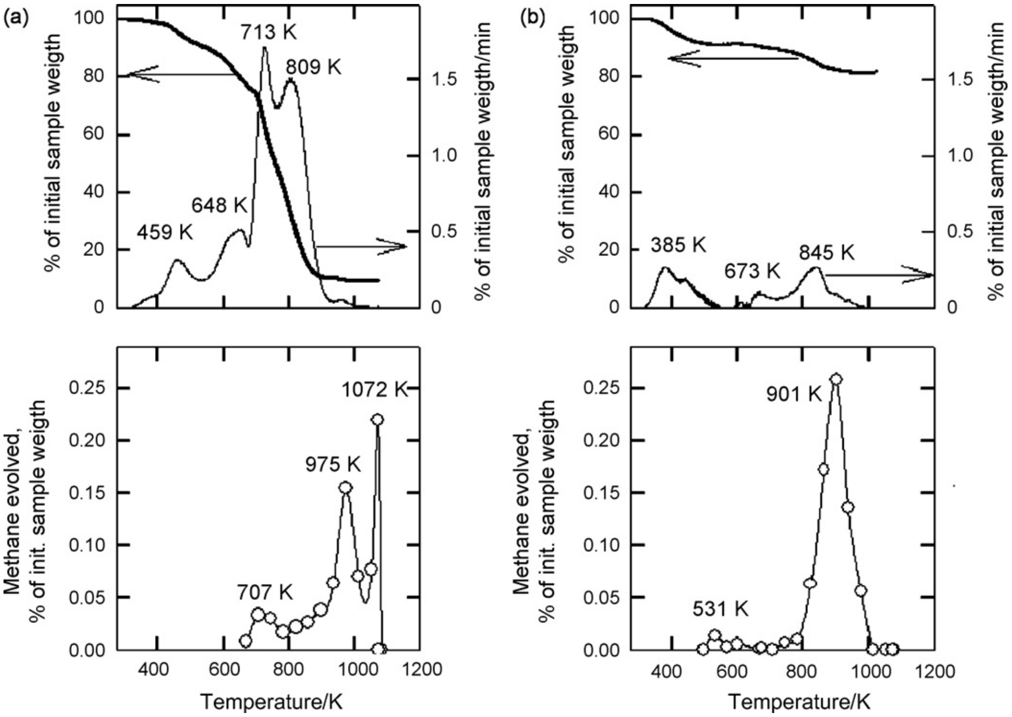

Fig. 11. Thermal decomposition of POTMD (a) and laser-derived hybrid (b).

3.6. *Thermal degradation of poly[oxy(tetramethyldisilane-1,2-diyl)] (POTMD) and laser-derived analogue*

Pulsed IR laser-induced ablation of poly[oxy(tetramethyldisilane-1,2-diyl)] leads to deposition of thin polyoxocarbosilane films with the backbone consisting of Si-methyl-substituted –SiSiO– and –OSiO– units and crosslinked through $SiSiC_2O$, C_3SiO, C_2SiHO, $CSiHO_2$ and $CSiO_3$ interlinks [17]. This laser product is a hybrid of siloxanes and polysilylenes. The TGA of POTMD (lab-synthesized sample, 38 mg) and of the laser-deposited polymer (3 mg) was performed by heating in Ar gas to 860 °C at the rate of 3.6 °C/min. The laser-fabricated hybrid remarkably differs from thermally unstable POTMD and shows superior thermal behaviour (Fig. 11).

While the decomposition of POTMD reaches four maxima at 459, 648, 713 and 809 K and leads to a black carbonaceous residue (only ca. 10 wt% of the initial sample), that of the laser-derived hybrid has three maxima at 385, 673 and 845 K and results in a whitish residue (83 wt% of the initial sample). The methane evolution during TGA of both samples is also very different. The laser-derived hybrid is thus revealed as withstanding temperatures of up to almost 800 °C. Its superior thermal stability was ascribed to the cross-linked struc-

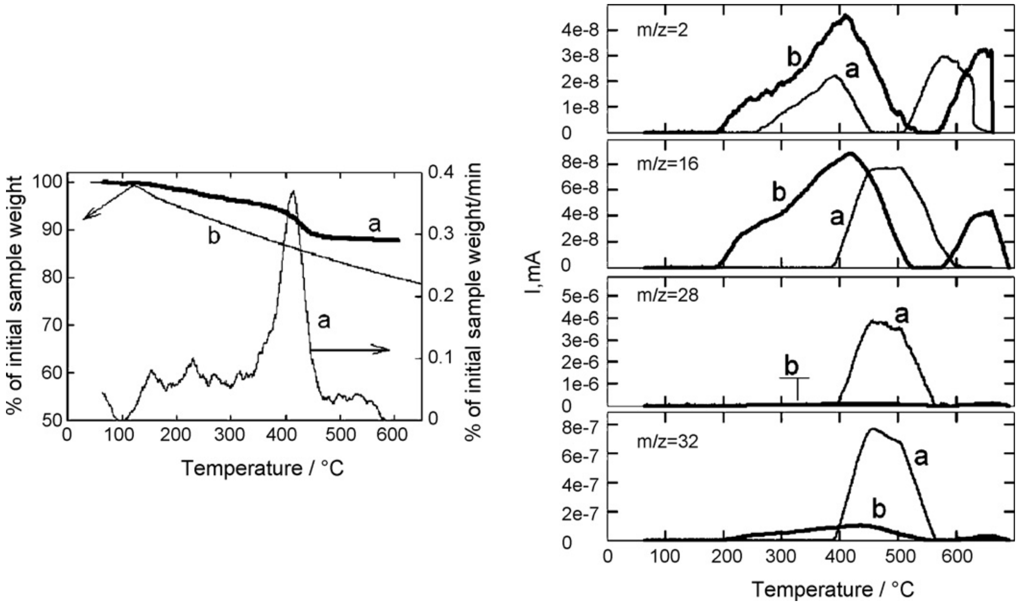

Fig. 12. Thermogram of ArF laser (a) and KrF laser (b) deposited materials and corresponding single-ion traces for H_2 ($m/z = 2$), CH_4 ($m/z = 16$), CO ($m/z = 28$) and CH_3OH ($m/z = 32$).

ture preventing extrusion of oligomeric parts which is so easy from linear polysilylenes and polysiloxanes.

3.7. Thermal degradation of carbon/polyoxocarbosilane composite

ArF and KrF laser-induced photolysis of gaseous toluene adjacent to silica leads to chemical vapour deposition of ultralight powders of amorphous and nanosized carbon/polyoxocarbosilane composites [18]. The process involves gas-phase etching of silica by hot carbonaceous fragments and has a potential for production of novel nanocomposite materials. The deposited composites experience different properties and thermal behaviour. The ArF laser-deposited material is diamagnetic, high-surface area and Si/O-rich composite, whereas the KrF laser-deposited material is ferromagnetic, low-surface area and Si/O-poor composite. The TGA of both samples (0.5 mg) was carried out by heating to 600 °C at the rate of 4 °C/min in a stream of Ar.

Thermograms of both materials are given in Fig. 12. The Si/O-rich composite shows a weight decrease at 400 °C, resembling thermal behaviour of highly crosslinked polysiloxanes, and major diagnostic single-ion traces of gaseous products corresponding to H_2, CH_4, CO and CH_3OH. The Si/O-poor composite experiences steady weight depletion and it liberates H_2 and CH_4 at temperatures starting from 200 °C.

This last example of TGA using only sub-mg sample quantities is illustrative of the high potential of the technique for complete elucidation of thermal behaviour of polymeric substances.

4. Conclusions

Thermal properties of low-quantity samples (thin films and ultrafine powders) of laser-produced polymers and polymeric composites can be feasibly measured by TGA coupled with GC and MS techniques. The method provides detailed information on the course of thermal degradation of polymeric substances which are available only in very low quantities.

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References

[1] A. Galíková, A. Galík, Proceedings of the 24th International Conference of the Slovak Society of Chemical Engineering, Častá-Papiernička, Slovakia, 1997.
[2] A. Galíková, A. Galík, Proceedings of the 25th International Conference of the Slovak Society of Chemical Engineering, Jasná, Demänovská dolina, Slovakia, 1998.
[3] A. Galík, A. Galíková, K. Klusáček, Chem. Eng. Sci. 54 (1999) 3495.
[4] A. Galíková, A. Galík, Chem. Pap. 55 (2001) 397.
[5] A. Galíková, A. Galík, J. Pola, Proceedings of the 29th International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, Slovakia, 2002.
[6] A. Galíková, J. Šubrt, Z. Bastl, J. Kupčík, J. Blazevska-Gilev, J. Pola, Thermochim. Acta 447 (2006) 75.
[7] J. Blazevska-Gilev, J. Kupčík, J. Šubrt, V. Vorlíček, A. Galíková, J. Pola, Polymer 46 (2005) 8973.
[8] J. Blazevska-Gilev, J. Kupčík, J. Šubrt, Z. Bastl, A. Galíková, J. Pola, Polym. Degrad. Stabil. 91 (2006) 2241.
[9] J. Blazevska-Gilev, J. Kupčík, J. Šubrt, Z. Bastl, V. Vorlíček, A. Galíková, D. Spaseska, J. Pola, Polym. Degrad. Stabil. 91 (2006) 213.
[10] J. Pola, A. Ouchi, Z. Bastl, J. Šubrt, M. Sakuragi, A. Galíková, A. Galík, Chem. Vap. Depos. 7 (2001) 19.
[11] J. Pola, A. Galíková, A. Galík, V. Blechta, Z. Bastl, J. Šubrt, A. Ouchi, Chem. Mater. 14 (2002) 144.
[12] J. Pola, R. Tomovska, S. Bakardjieva, A. Galíková, K. Vacek, A. Galík, J. Non-Cryst. Solids 328 (2003) 227.
[13] S.M.A. Durani, E.E. Khawaja, H.M. Masoudi, Z. Bastl, J. Šubrt, A. Galíková, J. Pola, J. Anal. Appl. Pyrol. 73 (2005) 145.
[14] J. Pola, A. Galíková, Z. Bastl, J. Šubrt, K. Vacek, J. Brus, A. Ouchi, Appl. Organomet. Chem. 20 (2006) 648.
[15] A. Galíková, Z. Bastl, R. Alexandrescu, I. Morjan, J. Pola, Thermochim. Acta 439 (2005) 80.
[16] M. Urbanová, J. Šubrt, A. Galíková, J. Pola, Polym. Degrad. Stabil. 91 (2006) 2318.
[17] J. Pola, J. Kupčík, V. Blechta, A. Galíková, A. Galík, J. Šubrt, J. Kurjata, J. Chojnowski, J. Chem. Mater. 14 (2002) 1242.
[18] J. Pola, S. Bakardjieva, M. Maryško, V. Vorlíček, J. Šubrt, Z. Bastl, A. Galíková, A. Ouchi, J. Phys. Chem. C 111 (2007) 16818.