COMPLEMENTARY DSC AND DILATOMETRIC INVESTIGATION OF M-PTFE PYROTECHNIC COMPOSITIONS

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Abstract

Results of high thermal resolution microcalorimetric and dilatometric measurements performed on reducer – polytetrafluoroethylene (M-PTFE) pyrotechnic compositions have been discussed. The materials were selected for the study because of their behaviour in combustion tests. Two complementary thermal properties, i.e. the specific heat and coefficient of linear thermal expansion (CLTE), have been analysed in detail. The specific heat was obtained from DSC measurements performed from –20 to 375°C. Measurements of CLTE and linear expansion were carried out from – 40 to 270°C. In both cases the measurements were performed on thermocycling with the high thermal resolution preserved. A special attention has been paid to a two-stage phase transition occurring just below the room temperature.

Keywords: DSC, laser interferometry, PTFE pyrotechnic mixtures, specific heat, thermal expansion

Introduction

Pyrotechnic composition based on polytetrafluoroethylene (PTFE) as oxidiser and different metallic powders as reducers (*M*) are condensed systems with very promising applications. The applications are connected mostly with highly exothermic chemical reactions occurring during combustion of these mixtures. The most common is their utilisation in flares and igniters. However, the latest findings show that M-PTFE pyrotechnic compositions should also be considered as an inexpensive source of carbon and inorganic nanostructures [1]. Because the combustion reaction course is strongly dependent on the reactant type, particle size and concentration, there is a possibility of passive control over it [2, 3]. But reliable analysis and effective optimisation of such processes require precise data on thermophysical properties of the reacting media. Preliminary investigations of basic thermal properties indicated a need for a wider and more thorough study in this domain [4, 5]. It seems that the attention should be focused on the structure and structure dependent thermal properties.

A unique opportunity for gathering information on thermal behaviour of M-PTFE pyrotechnic compositions is created by high thermal resolution investigation

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of specific heat and thermal expansivity. From a phenomenological point of view specific heat is a strictly thermal parameter while thermal expansivity is of thermomechanical nature. Despite the fact that the first one is a scalar, while the second is a tensor these two properties are closely related to each other both theoretically and experimentally [6, 7]. In addition, the thermal expansivity seems to be more influenced to the structure of materials than heat capacity [8]. Heat capacity exhibits more averaging behaviour if heterogeneous systems are considered (e.g. [4]).

In the present case thermophysical data (enthalpy, specific heat, coefficient of linear thermal expansion CLTE and thermal expansion) for pyrotechnic mixtures has been determined by microcalorimetric (DSC – differential scanning calorimetry) and dilatometric (HRLD – high (thermal) resolution laser dilatometry) studies. Investigations have been performed on four compositions and a pure PTFE. The methodology and the results of investigations are described below.

Experimental

Specimen material and preparation

The analysis was performed for four two-component M-PTFE mixtures consisting of PTFE and different 'metallic' powders (M = Zn, Al_3Mg_4, $CaSi_2$; these are metal and intermetallic compounds) and on pure PTFE. The powder material in PTFE matrix plays the role of reducing agent. Three of the investigated materials are novel, which means that they have not been considered and tested as pyrotechnic compositions before. This applies to compositions containing 76.7 mass% Zn, 56.7 mass% Zn and 52.8 mass% $CaSi_2$, the rest PTFE. The other one was composed of 54.5 mass% Al_3Mg_4, the rest PTFE. Specification of the investigated materials is provided together with selected results of measurements in Table 1. The investigated compositions were prepared by mixing the powdery M component and PTFE powder and cold-pressing then under the pressure of about 70 MPa. The PTFE powder (40 μm particle size) was a commercial grade (TARFLEN SM1) obtained from its producer Tarnow Chemical Plant S.A. The crystallinity of such materials at the delivery state should be about 93–98% [9]. According to deliverers' certificates, zinc powder (Merck) was of particle sizes below 5 μm while calcium silicide (Fluka) and magnalium (PAM4 – Trzebinia Metal Works) powders were of particle sizes below 100 μm. They contained more than 95% of the main ingredient. The specimens for DSC studies were cut out of thin disk plates (0.5–1.0 mm) and encapsulated in aluminium sample pans (Fig. 1a). On the very same disk plates density measurements had been made before (comp. [4]). Samples for dilatometric investigations were prepared in their final form of a hollow cylinder 12 mm in diameter, 8 mm in bore diameter, 10–20 mm high (Fig. 1b).

DSC measurements

Microcalorimetric investigations were carried out with a Perkin Elmer Pyris 1 DSC equipped with Intracooler 1 system. The measurements of enthalpy and specific heat
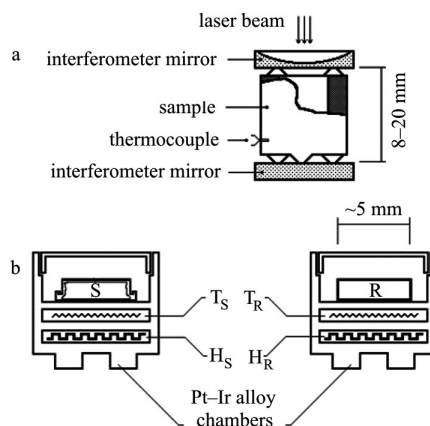
Fig. 1 Configuration of the investigated specimens: a – DSC measurements,
b – laser interferometry measurements

were done according to different thermal programmes but in both cases with thermal cycling. This means that the results of repeated heating and cooling cycles were analysed. The instrument was calibrated and the process was optimised for the heating rate of 20 K min^{-1}. However, for the Intracooler 1 system such a high cooling rate could not be applied to measurements at temperatures below 25°C. Therefore different heating/cooling rates were used for different thermal programmes. Compatibility of the obtained results was checked in every single case. A dynamic dehydrated N$_2$ atmosphere with a flow rate 20 mL min^{-1} was employed. The investigated specimens were encapsulated in aluminium sample pans of mass around 26.5 mg, whereas the investigated specimens masses ranged from about 20 to about 35 mg.

Thermal characteristics of the specific heat c_p were obtained by using a ratio method (a three-curve method; [10]). A 60.33 mg sapphire in the shape of a disk, about 5 mm in diameter and about 1 mm thick, similar to that of test specimens, was used as a reference specimen. Measurements were performed in a step scan mode – the thermal programme was composed of heating/cooling ramps interrupted by 1 min isotherms at: 25, 75, 125, 175, 225 and 275°C with 4 min extreme isotherms at –20 and 375°C. According to the literature data when the DSC instrument is correctly set up, overall accuracy better than ±1% can be reached [10]. This was confirmed in the test measurements performed with both step heating and cooling at temperatures from 0 to 660°C [8]. However, it should be mentioned that these experiments were performed on a Cu test specimen of a high thermal conductivity. A commonly accepted limit of uncertainty for routine DSC specific heat measurements is about ±2 to ±3%.

For the purpose of further comparative analysis some characteristic parameters of the observed low temperature phase transition were obtained from the obtained c_p curves. They were: the area of peak corresponding to the first stage of transition, the onset temperature of heating and the end temperature of cooling (Fig. 2) as well as c_p values at temperatures $t = -10$ and $t = 40$°C. Standard Pyris 1 software procedures were utilised in calculations.
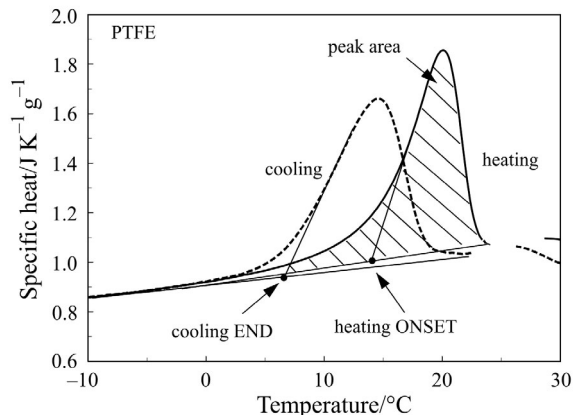
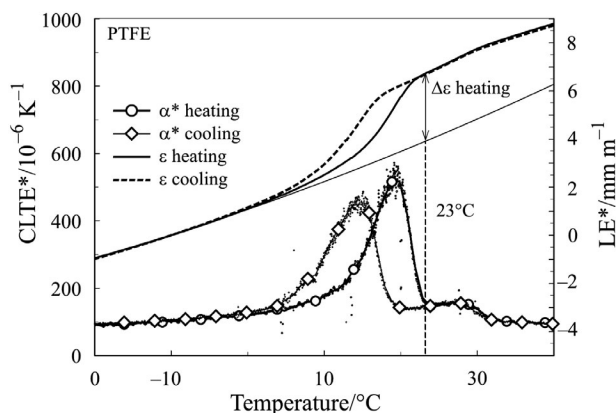**Fig. 2** Illustration of specific heat data processing: the example of PTFE results

Fig. 3 Illustration of dilatometric data processing: the example of PTFE

High thermal resolution laser dilatometry

Dilatometric measurements were performed using an absolute laser-interferometry apparatus with a microcomputer system for data acquisition and processing. A modified spherical interferometer was utilised (Fig. 1b). The apparatus enables high thermal resolution investigations of CLTE α and linear expansion ε (LE) within a temperature range from –130 to 1100°C. Specimens of various shapes can be tested. Details concerning the instrument design and methodology of measurements are provided in [7]. The actual resolution depends on many factors and affects the accuracy of CLTE determination. Both parameters are correlated and should be analysed together for every individual case. Test measurements performed for a Cu specimen within the range from 300 to 800 had shown that even if the resolution $\Delta T \cong 2$ K is preserved, the uncertainty could be less than 1% [7].

In the present case basic experiments were made within the range from about –40 to about 50°C and additional tests were performed from the room temperature to

about 270°C. Measurements were carried out in vacuum conditions on both heating and cooling over repeated temperature cycles. The heating/cooling rates were usually about 1 K min^{-1}. The specimen temperature was measured with a thermocouple of the K type (0.1 mm in diameter wire). The temperature sensor was attached to the side surface of the specimen. The upper horizontal surface of every specimen was cut to ensure a tripod support of the upper interferometer mirror (Fig. 1b).

The measured CLTE values were referred to the room temperature specimen length $l_0 = l(t_0 = 20°C)$ giving experimental standard values of $\alpha^*(t)$ [11]. The LE was calculated by integration of the $\alpha^*(t)$ curve. For the purpose of further analysis the obtained data was processed furthermore as it is shown in Fig. 3. Firstly the CLTE* results were averaged in 1 K intervals for the purpose of a clear presentation. It is because the raw data were of very high thermal resolution. In the case of exemplary PTFE results depicted in Fig. 3 the ΔT was ranged from about 0.15 K at –20°C to about 0.03 K within the region of the most intense transition changes at about 19.8°C. Secondly the LE results were recalculated to the level of $\varepsilon = 0$ at $t = –10°C$ in order to move the reference point outside the transition region. Next, the $\Delta\varepsilon$ was determined by

$$\Delta\varepsilon = \varepsilon_{\text{heating}}(t_1) - f_{\text{par}}(t_1) \tag{1}$$

where f was a parabolic extrapolation of the heating LE low temperature data from within [– 40,–10°C] and t_1 was equal to 23°C. This parameter is equivalent to the heating CLTE* peak area and can be juxtaposed to the heating c_p peak area. The whole procedure was completed with selecting characteristic α^* value at –10°C and ε at 40°C i.e. from outside the observed low temperature phase transition region.

Results and discussion

As was stated before the present investigations complement the results of basic thermal properties studies described in [4, 5], as well as some results of thermochemical analysis performed in [2]. Because of the fact of comparing thermal and thermo-mechanical properties the attention was focused on low temperature behaviour of compositions. It was impossible to conduct dilatometric measurements above the PTFE melting (onset at about 334°C, end at about 352°C – DSC data). However, some DSC results from the region up to 370°C and dilatometric results from the region up to 270°C are presented also. The measurements proved that properties of the investigated compositions were affected mostly by PTFE thermal behaviour. This concerns mainly thermal cycling behaviour. For that reason some typical phenomena will be illustrated with pure PTFE results only.

DSC specific heat measurements

Microcalorimetric measurements established thermal characteristics of specific heat changes. Selected results are shown in Figs 4–6 while some characteristic parameters are listed in Table 1. Typical behaviour of the investigated specimens under thermal cycling is illustrated with results of PTFE investigation. The measurements revealed

Table 1 Specification of the investigated specimens and characteristic parameters calculated from the obtained thermal characteristics[1] of $c_p(t)$, $\alpha^*(t)$ and $\varepsilon(t)$

	Zn76.7-PTFE	Zn56.7-PTFE	Al$_3$Mg$_4$-PTFE	CaSi$_2$-PTFE	PTFE
PTFE fraction/mass%	23.300	43.300	45.500	52.800	100.000
Density[2] at 20°C/Mg m^3	4.706	3.616	2.149	2.370	2.197
$c_p(-10°C)$/J g^{-1} K^{-1}	0.493	0.592	0.893	0.763	0.857
$c_p(40°C)$/J g^{-1} K^{-1}	0.523	0.637	0.952	0.813	0.963
$t_{heat\ ONSET}$/°C	12.840	13.293	12.782	13.086	14.416
$t_{cool\ END}$/°C	4.918	5.676	4.676	4.757	6.936
$c_{p\ peak\ area}$[3]/J g^{-1}	1.110	2.185	2.105	2.145	4.520
$\alpha^*(-10°C)\cdot 10^6$/K^{-1}	75.900	81.800	58.400	49.500	101.300
$\varepsilon(40°C)\cdot 10^3$	6.249	6.540	4.772	4.255	8.804
$\Delta\varepsilon(23°C)\cdot 10^3$	1.561	1.906	1.158	1.282	2.814
$\Delta\varepsilon/\varepsilon$ at 23°C	0.326	0.380	0.333	0.405	0.420

[1]In the case of Pyris 1 software the results are presented as they were obtained – with no correction for the actual accuracy
[2]Data from [4]
[3]Equivalent to the excessive change Δh in the measured specific free enthalpy.

two distinct phase transitions in the investigated temperature range. The first was observed at room temperatures and below. It was a solid–solid transition described in [9]. The transition was attributed to two-stage changes in torsion of PTFE chains. In this particular case the image of the second transition stage from within [23, 30°C] was disturbed by the vicinity of the 25°C isotherm stage of the applied DSC thermal programme. However, even results from the first stage could be applied in further analysis. The second transition, which was attributed to melting of the PTFE (a solid–liquid phase transition; Fig. 5), was discussed in detail in [4]. The measurements revealed effects of high temperature thermal cycling on specific heat characteristics. From the analysis of Figs 4 and 5 a conclusion could be drawn that increased values of first melting enthalpy might be connected with decreased c_p values on first heating. The decrease of the enthalpy of melting and melting onset temperature indicates that the changes are of structural nature and that they could be attributed to changes in the crystallinity. According to the literature the degree of crystallinity of annealed PTFE could be lowered even below 50% [9].

All the obtained characteristics are compared in Fig. 6 showing low temperature changes of specific heat. The figure can be used to estimate how the metal type and metal contents influence thermal properties of a given M-PTFE pyrotechnic mixture. In general, a conclusion can be drawn that thermal properties of compositions are determined mostly by properties of PTFE matrix. However, there is impossible to establish simple correlation between properties and PTFE contents. A detailed analysis revealed deviations from a simple rule of mixtures exceeding the expected uncertainty of measurements. This concerns the Al_3Mg_4 54.7 – PTFE composition in specific heat prediction (15% excess with reference to the theory – comp. [4]) and the two investigated Zn-PTFE compositions in c_p predictions (almost 30% lower experimental values [4]). The deviation seems not to be the case if the calculated values of c_p peak area is concerned (Table 1, Fig. 11). It should be noticed that differences between heating and cooling characteristics and thermal cycling effects were not so distinct as in the high temperature transition.
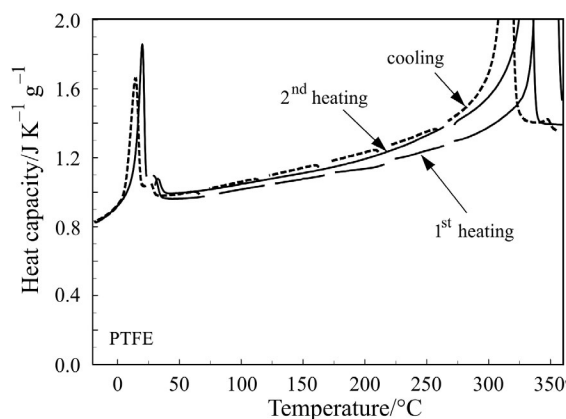

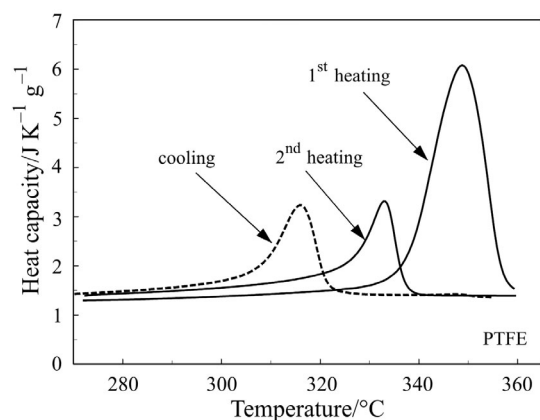**Fig. 4** Results of c_p of PTFE investigation under thermal cycling

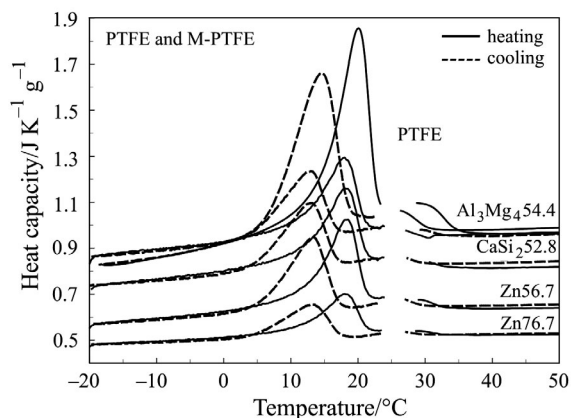**Fig. 5** A detailed illustration of results of DSC investigation of PTFE melting

Fig. 6 Comparison between results of DSC investigations at low temperatures

Dilatometric investigations

Dilatometric measurements established thermal characteristics of coefficient of linear thermal expansion α^* and dilatation ε. Selected, typical results are depicted in Figs 7–9. Characteristic parameters, derived from experimental curves, are listed in Table 1. The same as in the case of DSC studies the measurements proved that thermomechanical behaviour of the investigated pyrotechnic mixtures is shaped mostly by PTFE. Typical results of wide temperature PTFE dilatometric measurements are shown in Fig. 7. The observed effect of high temperature thermal cycling on linear expansivity revealed to be intensified with reference to the differences observed in specific heat. However, the effect of thermal ageing was reversed with reference to that disclosed in specific heat thermal characteristics. The α^* showed to be lower on both cooling and in heating cycles following the previous ones for about 40%. This phenomenon is accompanied by hysteresis in dilatation of every high temperature first run.
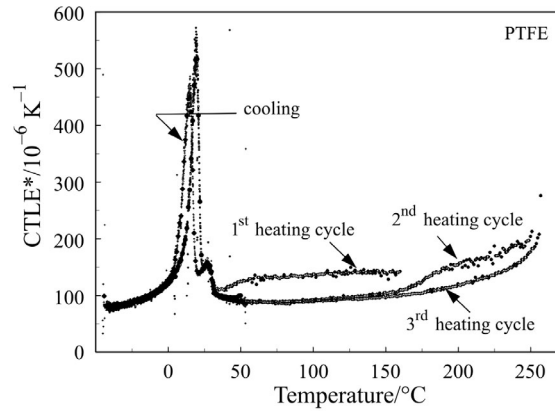
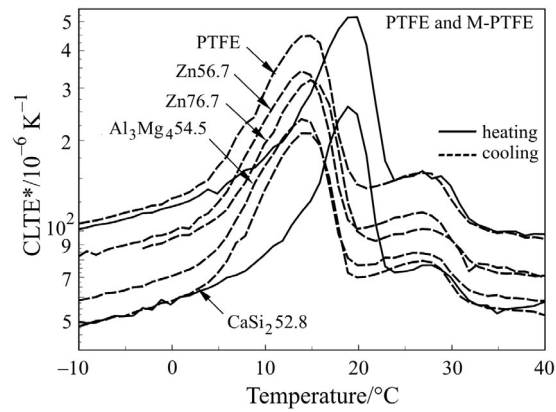**Fig. 7** Thermal expansivity of PTFE under thermal cycling

Fig. 8 Selected results of dilatometric investigations under low temperature thermal cycling: CLTE* data
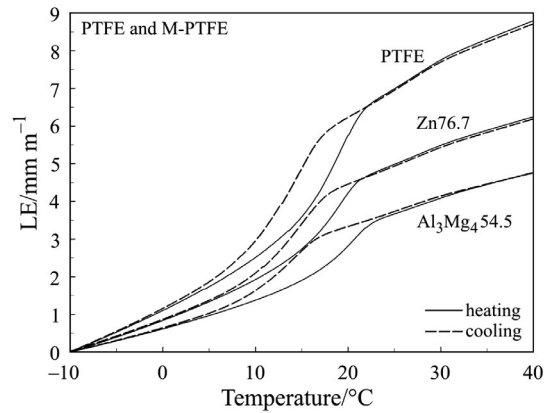

Fig. 9 Selected results of dilatometric investigations under low temperature thermal cycling: LE data

Selected characteristics of CLTE* and LE are compared in the low temperature phase transition region (Figs 8 and 9). When commenting on the results surprisingly high values obtained for the two Zn-PTFE mixtures should be pointed out. The observation confirms findings concerning strange thermal transport behaviour of the discussed two compositions from [4, 5]. Dilatometric measurements gave a clear picture of a low temperature phase transition. An interesting phenomenon concerning the second stage of the transition was revealed. This stage seemed not to be affected by subcooling effects. In general corresponding CLTE* heating and cooling characteristics overlap each other within the region [23, 30°C].

It is worth mentioning that an attempt was made to benefit from a high viscosity of polytetrafluoroethylene and cover the range of PTFE melting transition with dilatometric measurements. However, the intensity of length changes in pure PTFE revealed to be too high to ensure continuous recording of signals. Measurements performed on specimen of lower expansivity, the Zn76.7-PTFE one, failed due to self-ignition of the composition at about 360°C. It was far below the 550°C limit stated in DTA investigations [2]. The phenomenon have not been explained yet.

Comparison of DSC and HRLD results

In general the measurements confirm theoretical expectations of compatibility between specific heat and thermal expansivity. An example of comparison of DSC and HRLI results is presented in Fig. 10. Characteristics of c_p and α^* exhibit similar changes due to the temperature change. However, the linear expansivity proved to be more influenced by the structure changes than the specific heat. For example, changes in the specimen length in the region of low temperature transitions were intensified at least 5 times while the heat flux was increased only for about 60%. The intensity of changes is strongly dependent on PTFE fraction (compare Figs 6 and 8).

The two discussed techniques complement each other with results. This concerns not only the break in c_p results around 25°C but additional parameters calculated from the ob-
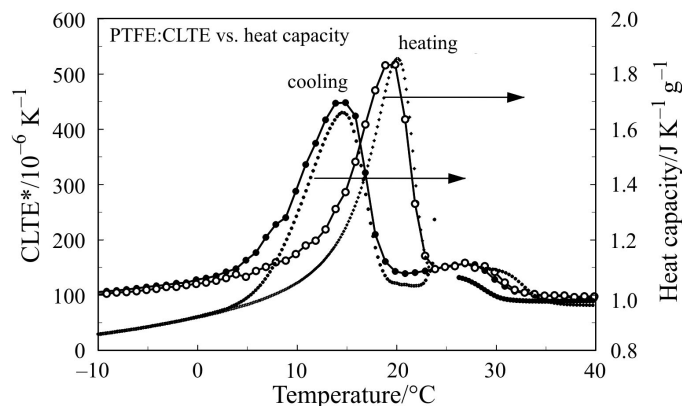

Fig. 10 Comparison between dilatometric and DSC results within the region of the low temperature transition of PTFE
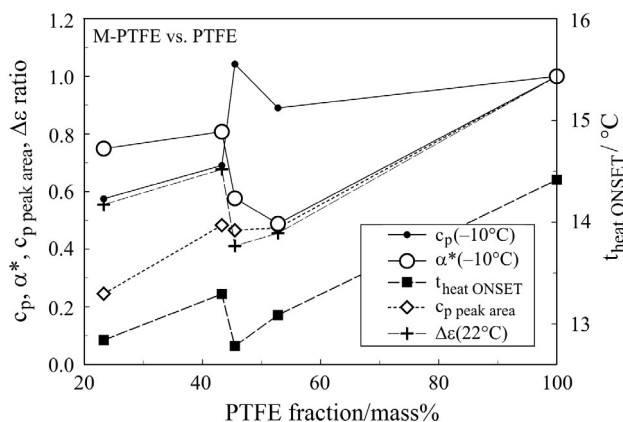
Fig. 11 Correlation between selected parameters (c_p, α^*, peak area and $\Delta\varepsilon$ referred to the pure PTFE values – comp. Table 1) of the investigated pyrotechnic compositions. Every specimen can be recognised by the mass fraction of PTFE

tained characteristics. However, the DSC measurements should be repeated with the isotherm removed from the whole region of the PTFE low temperature phase transition.

Interesting observations can be made when selected results from Table 1 are plotted *vs.* the mass fraction of PTFE. Despite the fact that quantitative conclusions regarding the rule of mixtures can not be directly drawn, the picture analysis indicated some deviations which were revealed in the thermal expansivity of Zn-PTFE mixtures. The observation confirms results of the density analysis performed in [4] and complies with strange thermal transport behaviour of the discussed pyrotechnics (deviations in thermal diffusivity – comp. [4], and [5]). But the most interesting is a strict correlation between characteristic temperatures (heating onset and cooling end), specific heat peak area and the excess dilatation $\Delta\varepsilon$. The disclosed phenomenon suggests that deviations of both thermal transport properties and some thermochemical properties (compare e.g. [2]) might be strongly dependent on the physical structure of the investigated compositions – the analysed properties seems to be affected by metal particle sizes, the impurity content, the state of M-PTFE interfacial surface, etc.

Conclusions

The high thermal resolution microcalorimetric and dilatometric investigations have been performed on selected M-PTFE pyrotechnic compositions and on pure PTFE. The attention was focused on a low temperature region over a solid–solid phase transition which occurs in PTFE or PTFE matrix. The results of measurements of different types complement each other. For the purpose of comparison of results a modified methodology of the experimental data processing have been proposed and successfully applied. The studies proved advantages of complex complementary investigations of thermal properties.

The results also substantially complement findings of previous investigations of thermal, thermochemical and thermal transport properties of the investigated materials.

The most important conclusion from the analysis of the obtained data concerns indications of structural effects on the thermal diffusivity and burning rate. The obtained results contribute to better understanding of combustion processes of the investigated pyrotechnics. The observations made can be used both in theoretical considerations and as a base for improving the methodology of measurements. In particular it is worth repeating low temperature DSC measurements to obtain more clear view of the solid–solid phase transition. However, any future analysis also needs more data on the thermal diffusivity or thermal conductivity of the discussed materials.

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