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THERMAL DECOMPOSITION OF PTFE IN THE PRESENCE OF SILICON, CALCIUM SILICIDE, FERROSILICON AND IRON

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Abstract

Simultaneous TG/DTA has been used to study the thermal decomposition of binary compositions containing polytetrafluoroethene (PTFE) with silicon (Si), calcium silicide ($CaSi_2$), ferrosilicon (FeSi) or iron (Fe) powders. In nitrogen and under dynamic heating program the thermal decomposition of Si/PTFE and $CaSi_2$/PTFE is an exothermic process. The other two compositions decompose endothermically. In each case the decomposition reactions show first-order kinetics but only iron does not change considerably the kinetics of PTFE depolymerization. The constants of the decomposition rate at 850 K for silicon containing reducers are about four times higher than those of PTFE and Fe/PTFE.

Keywords: kinetics, silicon-PTFE mixtures, TG/DTA, thermal decomposition

Introduction

Despite the fact that PTFE is chemically and thermally resistant, owing in part to the high energy of the C–F bond, it can still be used as an oxidizing agent, since for many metals the metal-fluorine bond strength is even greater than that of the C–F bond. Therefore some of the metal/PTFE mixtures are highly energetic materials that are widely known in the pyrotechnic community for their effectiveness and performance in flare and igniter applications [1]. Less recognised, though, is the fact that these compositions can be a source of polymeric carbon [2, 3] as well as novel carbon and ceramic nanostructures which are produced in highly exothermic ultra-fast chemical reactions at very high temperatures during combustion of the mixtures [4]. Because of the fact that the reaction course is strongly dependent on the reactant type, particle size and concentration, there is a possibility of passive control over it. But reliable analysis and effective optimisation of such processes need precise data on the characteristic temperatures and the kinetic parameters of the PTFE thermal decomposition in the presence of different reducers.

In the present work simultaneous TG/DTA was used to determine the kinetic parameters of the thermolysis of PTFE in binary mixtures with silicon, calcium silicide,

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ferrosilicon and iron. The results obtained were also applied for an evaluation of the reactivity of the reducers towards PTFE and its decomposition products.

Experimental

Simultaneous TG/DTA experiments were performed using a MOM Hungary Derivatograph-PC. In general runs were carried out using matched labyrinth platinic crucibles with Al_2O_3 in the reference pan. The crucible design hampered the migration of the volatile decomposition products reducing the rate of gas evolution and, in turn, increasing contact time of the reactants. All the DTA curves were obtained at 10 K min^{-1} heating rate with a nitrogen dynamic atmosphere (flow rate 20 dm^3 h^{-1}).

The tests were conducted for PTFE and its mixtures (50/50 by mass) with the reducers. Samples (22–32 mg in mass) were in a form of a thin foil pressed at 500 MPa. PTFE powder (40 μm particle size) was a commercial grade (TARFLEN SM1) obtained from its producer Tarnow Chemical Plant S.A.. Silicon powder (MERCK), calcium silicide ($CaSi_2$), ferrosilicon (Fe/Si=30/70 by mass) and iron powders (all of them Fluka) contained more than 95% of the main ingredient. According to the deliverer certificates, particle sizes of the reducers were below 100 μm.

Results and discussion

Figure 1 illustrates TG/DTA curves for the samples tested. The first peak on the DTA curves (around 617 K) is due to the melting point of PTFE. At 770 K the mass loss of the samples equals to ca. 1% and that temperature was assumed as the beginning of the PTFE decomposition process. The DTA of the initial stage of PTFE degradation gives a small exotherm peaking at 820 and ending at 837 K. Next after a short but distinct stoppage, a large endotherm begins with the minimum occurring at 875 and the end at 920 K. The total mass loss at 900 K equals to ca. 97% thus the decomposition products are almost exclusively gases.

Mixtures containing Fe and FeSi behave quite similarly. Their decomposition is an endothermic process in the temperature range within which the mass losses take place. In the $CaSi_2$/PTFE mixture, exothermic reactions commence at about 700 K when the reactants are still in a condensed phase. Moreover calcium silicide causes an exotherm to develop at 800 K, but the endothermicity of PTFE degradation at higher temperatures is observed. Silicon does not react with PTFE below 770 K, however, it is capable to exothermic reactions with the gaseous PTFE decomposition products, and the sharp exotherm at 840 K results from the reactions.

An analysis of the decomposition kinetics was based on the TG curves. First they were transformed in temperature dependence of conversion degrees (α) defined as a ratio of current mass loss to the initial mass of PTFE in a sample. The time derivatives of the conversion degree ($d\alpha/dt$) as a function of temperature are shown in Fig. 2. It is apparent from Fig. 2 that PTFE and Fe/PTFE degrade in two mass loss stages, the maximum rates of which are separated by about 40 K. This is probably a

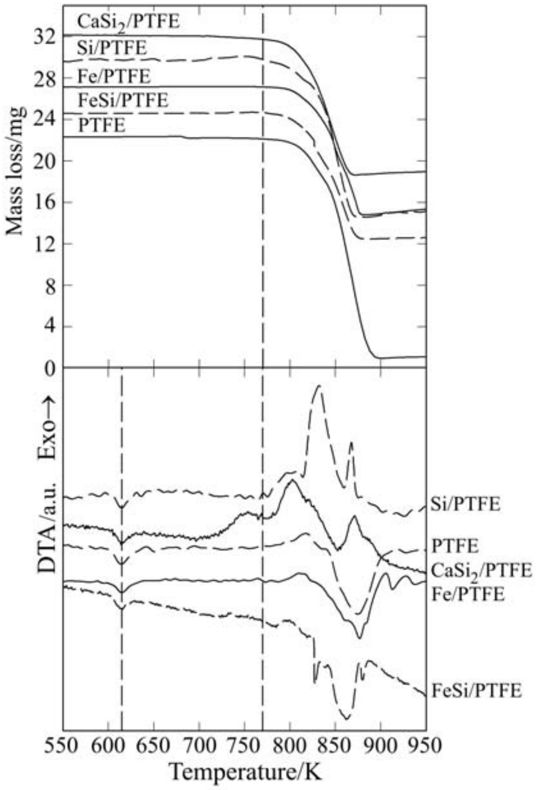

Fig. 1 TG/DTA curves of PTFE and its mixtures with Fe, Si, FeSi and $CaSi_2$

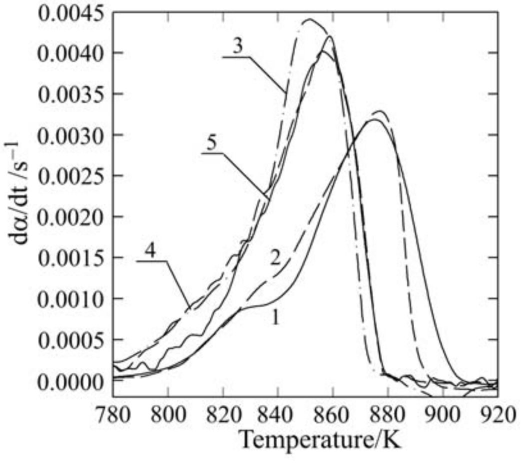

Fig. 2 Dependence of the mass loss rate on temperature for 1 – PTFE and its mixtures with 2 – Fe, 3 – Si, 4 – FeSi and 5 – $CaSi_2$

result of the radical decomposition mechanism of PTFE [5, 6]. Main-chain scission results in chains with radical ends, which can either undergo depolymerization or cyclization as well as crosslinking. The residue remaining after depolymerization stage is more thermally stable and degrades at higher temperatures. A small exothermic event is observed in the same temperature range as the first mass loss stage, but the endothermicity of the partially cyclized and crosslinked residue degradation soon masks any exothermic processes. In the presence of more chemically active reducers (containing silicon) depolymerization of PTFE is favoured over cyclization because of an additional energy produced by the chemical reactions in the mixture. Consequently the slow-down in the decomposition rate is not so clearly seen, and the maximum rate of decomposition occurs at a lower temperature of 850 K.

In order to rank the reactivity of the reducers towards PTFE, an analysis of the decomposition kinetics was carried out using simple kinetic models. The use of a one-constant model was conditioned on the accuracy of the measurement technique. Usefulness of first-order and second-order kinetics was checked, and the first model best fitted the experimental data. Figure 3 illustrates the Arrhenius plots obtained.

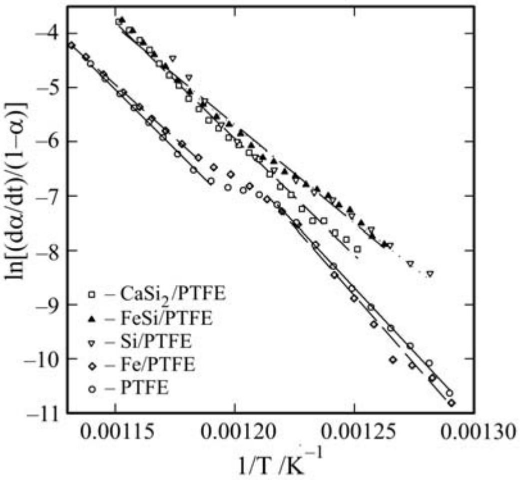

Fig. 3 Arrhenius plots from dα/d*t* data for PTFE and its mixtures with Fe, Si, FeSi and CaSi$_2$

For PTFE and Fe/PTFE two sets of kinetic parameters were determined using the low-temperature and high-temperature linear parts of the Arrhenius plots. Assuming that the mechanism of PTFE thermal decomposition described above is a correct one, the first set corresponds to the PTFE depolymerization and the second one characterises the decomposition of the cyclized and crosslinked material not undergoing depolymerization in the first stage. In the case of Si-containing samples, one equation describes the whole decomposition process with quite high correlation coefficients (r). Apparent activation energies (E_a), pre-exponential factors (A) and decomposition rate constants predicted for 850 K (k_{850}) are collected in Table 1. The activation energies of PTFE degradation obtained in the present work are between 287–394 kJ mol^{-1}. These values are in a quite good agreement with those of 275–349 kJ mol^{-1} reported in [5]. Iron does not practically change the kinetics of PTFE degradation. The influence of the other reducers is significant. They cause the constants of the mass loss rate predicted for 850 K to increase by three-four times as compared to the constant for PTFE, which was calculated using the high-temperature set of Arrhenius parameters. It should be pointed out that all the reducers containing silicon display comparable catalytic effect on the decomposition rate. This suggests similar mechanism (probably chemical one) of the acceleration of PTFE decomposition. Another fact worth mentioning is that the estimated activation energies of 350±48 kJ mol^{-1} are close to the energy needed for typical C–C bond scission of 350 kJ mol^{-1}. Since tetrafluoroethene is the major thermal decomposition product of PTFE [5], the activation energy should be close to the expected value for carbon chain scission.

Table 1 Arrhenius parameters (A, E_a) and rate constants at 850 K (k_{850}) for PTFE and its mixtures with the reducers

Sample	$\ln A$	E_a/kJ mol^{-1}	k_{850}/s^{-1}	Correlation coefficient/r
PTFE(l)	50.58	394.2	0.0055	0.999
PTFE(h)	45.76	367.2	0.0022	0.999
Fe/PTFE(l)	54.11	418.6	0.0059	0.995
Fe/PTFE(h)	40.58	329.2	0.0025	0.999
FeSi/PTFE	52.89	302.0	0.0080	0.992
Si/PTFE	35.77	287.5	0.0074	0.987
$CaSi_2$/PTFE	45.53	356.6	0.0072	0.995

(l) – low-temperature range, (h) – high-temperature range

Conclusions

From the results obtained the following conclusions can be drawn:

1) Thermal degradation of pure PTFE and its mixture with iron proceeds through two stages of mass loss. Iron does not change the kinetics of PTFE degradation because the rate constants predicted for 850 K are nearly the same for both samples and temperature ranges.

2) Thermal degradation of Si/PTFE composition is, in general, an exothermic process in the temperature range within which the mass losses take place. In the $CaSi_2$/PTFE system exothermic reactions occur at 700 K, but the endothermicity of PTFE degradation is still observed at the temperature of maximum rate of mass loss.

3) For mixtures with reducers containing silicon the decomposition is a one-stage process and its rate constants are about four times higher than that of PTFE in the high-temperature region. Similar catalytic effect of the Si-containing reducers suggests that silicon accelerates PTFE decomposition.

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