Combined thermal analysis and gas-analysis methods and software simulations for the investigation of the potential endangerment to the environment through production and recycling processes[1]

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Abstract

The application of coupled thermal analysis and gas-analysis instruments provides information on type and quantity of gases evolved during a technical production process. This was shown for ceramic firing processes and the curing of a phenolic resin. Kinetic analysis of degradation and decomposition reactions was applied to predict the long-term stability of a PVC compound and the rate-controlled burn-out of polymeric binders from alumina. An endangerment to the environment by atmospheric emissions can be estimated from the type and amount of gases detected and it has to be seen in comparison to the environmental legislation limits. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Binder burn-out; Coupled FTIR; Coupled MS; Gas analysis; Kinetics; Recycling; Stability prediction

1. Introduction

Production and recycling processes involving heat are well suited for study by methods of thermal analysis, where physical and chemical properties of a sample are measured during a controlled temperature programme. The environmental relevance of any of these processes is, in this concern, mostly characterised by the volatile products evolved into the surroundings. Therefore, gas-analysis methods coupled with thermal analysis are most informative for the detection of poisonous gases which are produced during a technical process and for the estima-

tion of endangerment to the environment. It can be shown that, with the knowledge of the kinetics of degradation and decomposition reactions, a prediction of the long-term stability of materials becomes possible and the danger of evolution of harmful substances at temperatures far below the normal short-term stability limits can be predicted.

2. Experimental

The special features of thermal analysis for material testing are listed in Table 1. This shows the versatility for qualitative material comparisons as well as for the quantitative measurement of thermophysical properties. The methods most frequently applied for the detection of weight changes of a material during heating are: thermogravimetry (TG) coupled with

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Table 1
Special features of thermal analysis for material testing

Topic	Information	Method
Quality-comparison	good/bad	all
Thermal stability	application limits	TG [d], DSC [e], DTA [g], DMA [d]
	influence of atmosphere	TG [d], TG-MS, TG-FTIR [i]
	decomposition products	TG-MS [k], TG-FTIR [i]
Identification	phase transitions	DSC [e], DTA [g]
Absolute data	temperature of transitions and reactions	DTA [g], DSC [e]
	heat of transitions	DSC [e]
	specific heat	DSC [e]
	expansion coefficient	TMA [f], DIL [a]
	elastic moduli	DMA [c]
	thermal conductivity	TCT [b]
	thermal diffusivity	laser-flash technique
	vapour pressure	VPA [h], VPB [j]

[a] Dilatometry.
[b] Thermal conductivity tester.
[c] Dynamic-mechanical analysis.
[d] Thermogravimetry.
[e] Differential scanning calorimetry.
[f] Thermomechanical analysis.
[g] Differential thermal analysis.
[h] Vapour pressure analysis.
[i] Fourier transform infrared spectroscopy.
[j] Vapour pressure balance.
[k] MS mass spectrometry.

gas-analysis techniques, such as mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR). Thus, nearly all volatile products evolved during a heating cycle are quantitatively measured at the temperature of evolution and continuously analysed for their composition. Nowadays, large samples can also be used in combined TG–MS for a representative analysis of the incineration process of waste or the characterisation of the production process of complete parts in powder-metallurgy or technical ceramics [1]. Vapour-pressure measurements allow the determination of the concentration of evolved species at work-stations and, therefore, an estimation of the damage to health from hazardous substances at surrounding temperatures [2].

The gas evolution during the firing processes of traditional and technical ceramics is analysed by combined TG-MS and TG-FTIR. Quadrupole mass spectrometers are directly coupled via the Skimmer and capillary coupling systems to the NETZSCH STA 409 and TG 209 thermobalances [3]. For the quanti-

fication of the detected gaseous products, the newly-introduced pulse thermal analysis technique (PTA) is applied [4,5]. The FTIR equipped with a heated gas measuring cell is coupled to the TG 209 via a flexible, heated transfer line. In the field of polymers, the thermal stability and gas evolution during curing reactions of phenolic resins, recycling of automobile undercoatings [6] and electronic waste [7] are studied. The long-term stability of a PVC compound is predicted using kinetic analysis for the plasticiser evolution and the degradation of the thermoplastic polymer. Combined TG-FTIR is also well suited for the analysis of the gases evolved at the processing temperature of thermoplastic materials, e.g. for polyoxymethylene (POM) [8].

The atmosphere for the tests in the combined instruments is mainly an inert gas flow, which prevents the complete destruction of organic volatiles, as would be the case under oxidative conditions. The gas flow must purge the sample chamber at the necessary rate to achieve short transfer times to the gas analysers.

3. Results and discussion

A traditional brick clay for roof tile production was analysed with the TG-FTIR coupling to show the gases evolved under the usual heating conditions according to the production process. The complex weight-loss behaviour during heating in air to 1000°C was discussed in [3] mainly for the detection of HF evolution at temperatures between 800°C and 1000°C. From the point of environmental protection one must consider a number of additional gases produced during this process of brick clay firing, which has been practised around the world almost since the domestication of mankind. Fig. 1 shows an overview of the temperature and time-dependent total gas production detected by the FTIR (Gram Schmidt plot) and the individual traces for H_2O, CO_2, CO, SO_2 and HF. The plots show the presence of the selected gases, but not their quantitative distribution in the evolved gas, as the scales for the IR absorption were not calibrated.

The oxidative condition during the firing process is not efficient enough to exclude the CO evolution from unburned organic matter. SO_2 is the decomposition product of sulphates and the oxidation product of sulphides contained in the clay. The conclusion from this relatively high effort for the analytical study of the process becomes evident, that either a modification of the mineral composition of the clays from natural resources, or a cleaning of the flue gases will lead to more environmentally friendly brick firing processes. It must be pointed out, that a careful selection of firing conditions could also lead to immobilisation of some of the hazardous gases released during brick firing [9]. The advantage of using thermal analysis combined with FTIR is the short time for getting results as compared to chemical methods, and the clear indication of HF evolution besides the water, which would not be clear from combined mass spectrometry because of the overlapping signals caused by isotope distribution.

Automated production technologies require the addition of mainly polymeric additives and binders to the natural raw materials, even for traditional ceramics. Although low concentrations are generally used, the decomposition products of these additives can contribute to hazardous and corrosive volatiles in the flue gas during the firing process [10].

The production of technical ceramics and powder-metallurgical parts is only possible with the aid of relatively high contents of organic additives and polymeric binders. Thermal analysis has various application goals, such as optimisation of the binder burn-out, determination of the best sintering conditions, and in this regard, identification of the gaseous decomposition products [11,12]. For mixtures of organic additives a preseparation of the decomposition ranges could be necessary for interpretation of the gas-analysis results. This preseparation is simplified with knowledge about the decomposition mechanisms, i.e. the kinetics of the burn-out process. Kinetic analysis of the complex decomposition reactions is now possible with a multiple scan kinetic programme, which uses several heating curves at different rates or isothermal curves simultaneously for the determination of one globally-valid reaction model [13].

The main steps in this kinetic analysis are listed in Table 2.

The application for the binder burn-out from alumina is demonstrated in Fig. 2. Six TG curves for heating rates between 0.1 and 10 K/min indicate nearly invariant weight loss of 9.3% in two steps over the 100–500°C range. The formal approximation of these experimental values is excellent using the complex reaction model of one independent reaction, A to B, and parallel to it a three-step consecutive reaction, C to F.

The kinetic parameters for this formal approximation are given in Table 3. Based on this global fit of the experiments, the conditions for a rate-controlled mass change (RCM) experiment can be calculated. This is a desirable condition for a smooth burn-out of the binder without danger of the moulded part cracking due to a too rapid gas production, and for a separate analysis of the gas composition. Fig. 3 shows the temperature curve for achieving a mass loss rate of 0.1%/min, determined via recalculation from the kinetic parameters.

The tabular printout of the temperature/time values allows the direct transfer of these conditions to the laboratory instrument or to the production furnace. The precise agreement between such predictions and experiments could be shown for rate-controlled sintering of alumina in a dilatometer [14].

An example for the identification of gases produced during the binder burn-out from another alumina
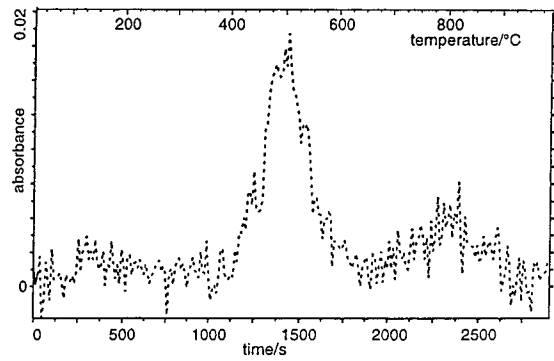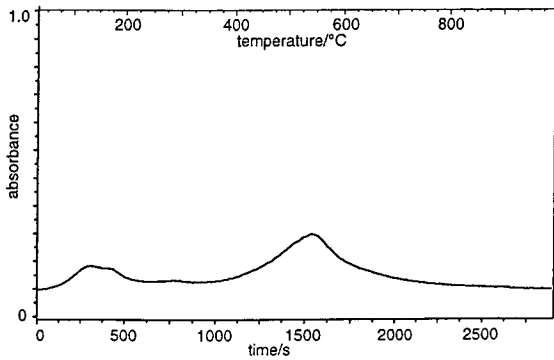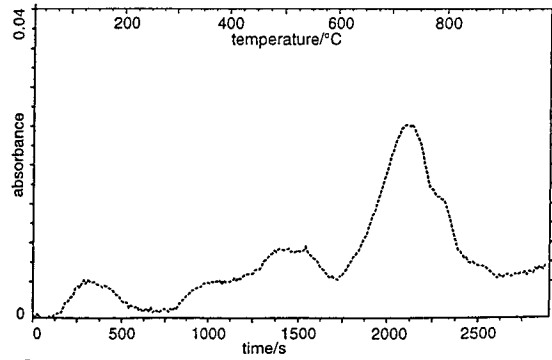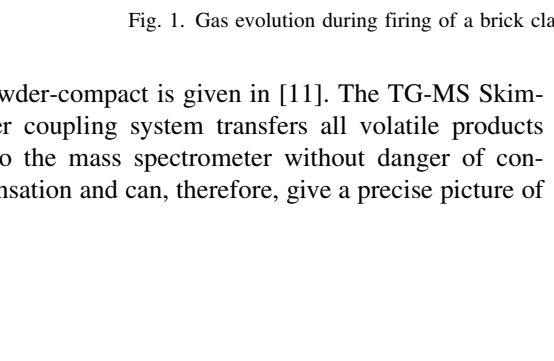
TG 209-FTIR
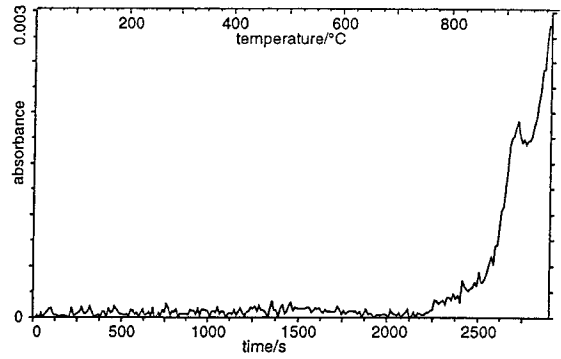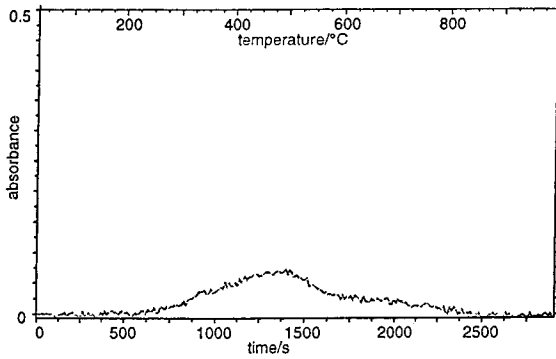
CO-trace
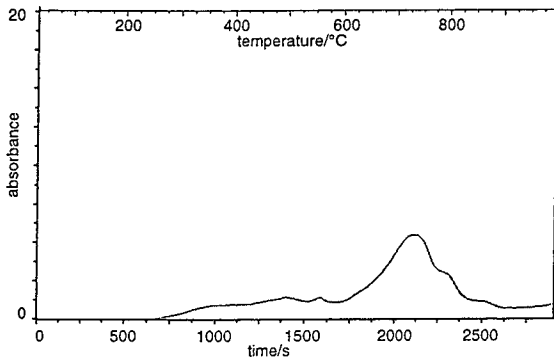
HF-trace

CO_2-trace

SO_2-trace

H_2O-trace

Gram-Schmidt

Fig. 1. Gas evolution during firing of a brick clay in coupled TG-FTIR, 94.51 mg, air flow, 20 K/min.

powder-compact is given in [11]. The TG-MS Skimmer coupling system transfers all volatile products into the mass spectrometer without danger of condensation and can, therefore, give a precise picture of

possible endangerment to the environment from the gases produced during binder burn-out.

In the polymeric field, the temperatures during production and moulding are much lower compared

Table 2
Main steps in multiple scan kinetic analysis

|	
1	Loading of ASCII files covering the reaction range (max. 8 curves, heating or isothermal)
2	Model-free analysis for orientation on the variation of the activation energy with degree of reaction (Friedman, Ozawa, Flynn, Wall)
3	Selection of kinetic model (max. 4 steps with individually selected mechanisms)
4	Multiple linear regressions for single step reactions
5	Nonlinear regression to find the best agreement between experiment and kinetic model (simultaneous evaluation of all curves)
6	Prediction of the reaction at user-defined conditions for time and temperature
7	Prediction of the reaction under rate-controlled conditions (RCM, RCS) with documentation of the temperature-time curve
8	Prediction of the reaction under user-defined temperature programmes
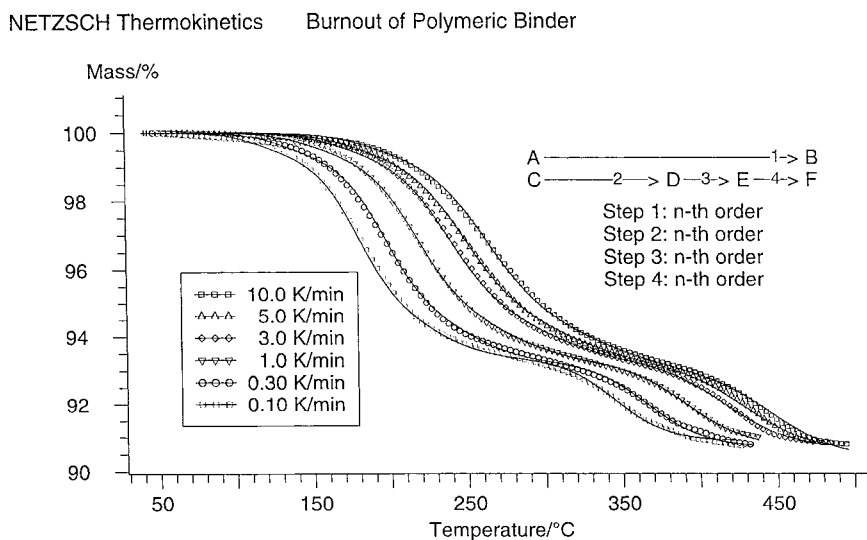
Fig. 2. Binder burn-out from alumina at different heating rates, approximation of experimental TG values by one kinetic model.

with ceramic firing processes. However, they can be close to the short-term stability limits, and application temperatures are often near the long-term stability limits. Initial decomposition of the polymer, but more often evaporation and decomposition of plasticisers and additives, are reasons for gas evolution from polymeric products.

The curing of thermosetting resins is often a process accompanied by gas evolution. Although a laboratory test does not completely simulate all conditions of a curing process on a technical scale, one can follow the gas production in a coupled TG-MS or TG-FTIR system. In particular, the curing of phenol-formaldehyde resins is a subject of study for the type and amount of gases evolved, mainly for the free formaldehyde, phenol and organic fragments. In Fig. 4, the neighbouring curing (100–200°C) and degradation

(240–640°C) reactions can be seen, with clear detection of formaldehyde (m/z 29) and water (m/z 18) during curing and, additionally, phenol (m/z 94) with the start of degradation.

Different types of phenol-formaldehyde resins exhibit significant differences in the amount of evolved formaldehyde and phenol during curing. These gases must be removed from production workstations for the protection of the employees.

It is reported that thermoplastic materials can also show gas evolution at the temperatures of an injection moulding process [8]. This could be simulated for poly-oxymethylene (POM) at the processing temperature in a combined TG-FTIR system, and formaldehyde was clearly detected for a certain type of POM.

The gas evolved at the start of the PVC decomposition is HCl in an autocatalytic reaction, which

Table 3
Kinetic parameters for the burn-out of polymeric binders

Step 1:	A	$\Rightarrow$	B
	contribution		0.71%
	$\log A$		=8.16
	$E/(kJ/mol)$		=90.1
	n		=2
Step 2:	C	$\Rightarrow$	D
	contribution		58.4%
	$\log A$		=7.79
	$E/(kJ/mol)$		=102.3
	n		=1.8
Step 3:	D	$\Rightarrow$	E
	contribution		12.8%
	$\log A$		=6.1
	$E/(kJ/mol)$		=98.9
	n		=1.7
Step 4:	E	$\Rightarrow$	F
	contribution		28.09%
	$\log A$		=9.48
	$E/(kJ/mol)$		=160.7
	n		=1.7

explains the bad image of this frequently used material from an environmental safety point of view. A PVC compound (with plasticisers) was studied at different heating rates with thermogravimetry to simulate, via a kinetic analysis, the weight stability under long-term conditions for storage or use. Fig. 5 represents the good approximation of the three multiple-step decomposition curves by the kinetic model (correlation coefficient 0.99987) in the temperature range of the plasticiser evolution and the first steps of the PVC decomposition.

With the so-called engineering plots from the kinetic analysis, one can predict the sample behaviour for selected temperature/time conditions. Looking at a temperature range of 100–150°C, which would be realistic for summer conditions in the interior of a car behind the windshields, one can see that the plasticisers evolve completely at 140°C and exposure times of 10 h (Fig. 6). This can lead to the well-known fogging effect on the windshield and often to the 'plastic smell' of new cars, if this kind of material is used.

Extending the calculation to 100 h, one can conclude that the decomposition of PVC starts at temperatures >140°C and leads to significant degradation even at 150°C after 20 h (Fig. 7).

These predictions from a kinetic analysis dramatically demonstrate the influence of the time factor on the stability of a polymer and, in the case of the PVC, the potential for the HCl evolution during long-term use, even at relatively low temperatures. The justification for a prediction must be a broad experimental base
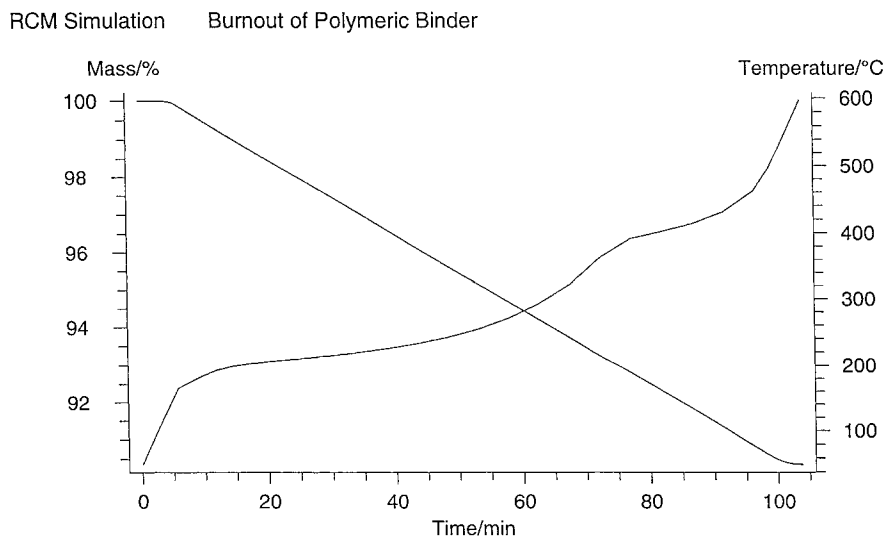

Fig. 3. Prediction of rate-controlled mass loss conditions (0.1%/min) using the kinetic model for binder burn-out from alumina.
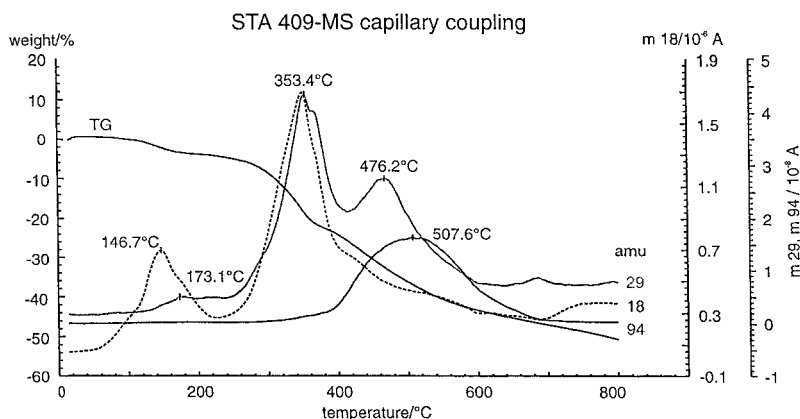
Fig. 4. Curing and degradation of phenolic resin measured with TG-MS capillary coupling; 30.52 mg, argon 250 ml/min, 10 K/min.
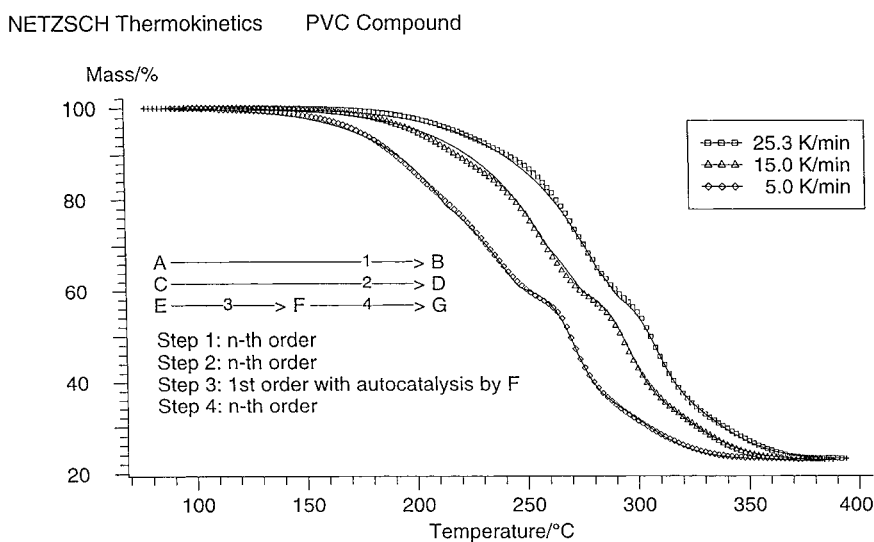
Fig. 5. Decomposition of a PVC compound with plasticisers, measured with TG at three heating rates, kinetic model and approximation; ca. 5 mg, nitrogen 20 ml/min

and a perfect, formal approximation of it by the kinetic model.

Recycling processes are well established for many materials. Besides the important studies for the identification of waste materials before they are subjected to a recycling process, it is equally important to study the volatiles produced during thermal recycling processes. This necessity is evident for waste incineration plants, but smaller scale processes must also be analysed. In case of recycling of heterogeneous products, gas analysis on a laboratory scale is important and

successful, as could be shown for electronic waste [10] and for automobile undercoating material [6].

Large molecular organic fragments were detected by the TG-MS Skimmer coupling during the pyrolysis of a polystyrene (Figs. 8 and 9). The frequent use of this type of polymer for thermal insulation materials in the building industry creates a future problem for recycling of the otherwise mostly inorganic building materials.

It was particularly interesting that the Skimmer coupling could detect not only the monomeric
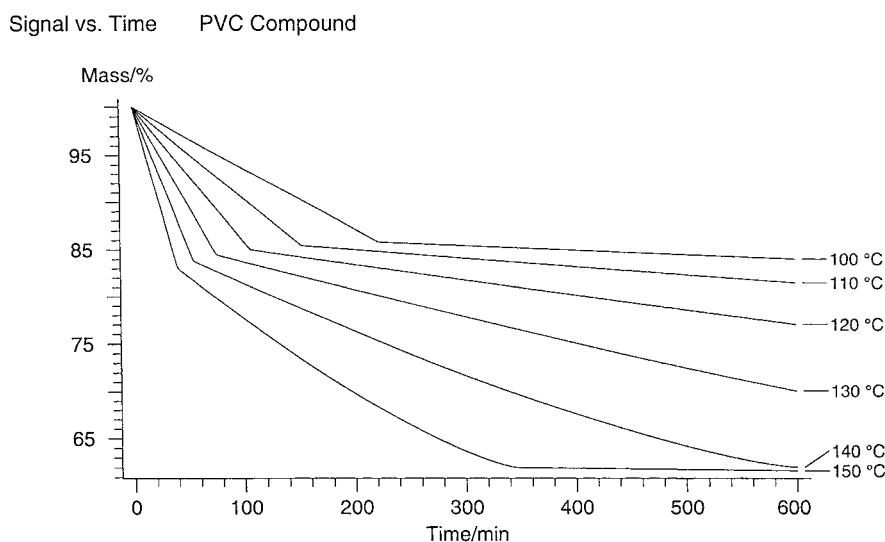
Signal vs. Time   PVC Compound

Fig. 6. Prediction of weight loss through plasticiser evaporation and decomposition for a PVC compound at isothermal conditions with the temperature as parameter, using the kinetic model.

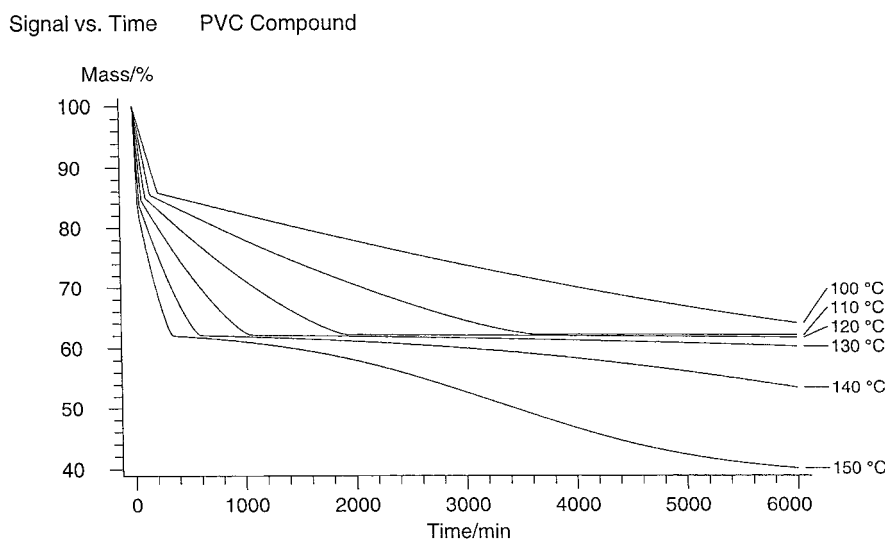Signal vs. Time   PVC Compound

Fig. 7. Long-term prediction of weight loss through plasticiser evaporation and PVC decomposition at isothermal conditions with the temperature as parameter, using the kinetic model.

styrene-fragment (*m/z* 104) and the aromatic fragments benzene and toluene usually found [15], but also two and three styrene repeating units with the mass numbers 208 and 312, respectively. Thermal dissociation and fragmentation by the electron impact ionisation in the mass spectrometer lead to a series of molecular fragments with mass numbers differing by 14, 15 and 28 amu from the two- and threefold repeating units, which is most clearly shown in Fig. 9.

For any thermal treatment of polymeric waste, the production of poisonous gases during the process must be carefully monitored, as can be concluded from the above.
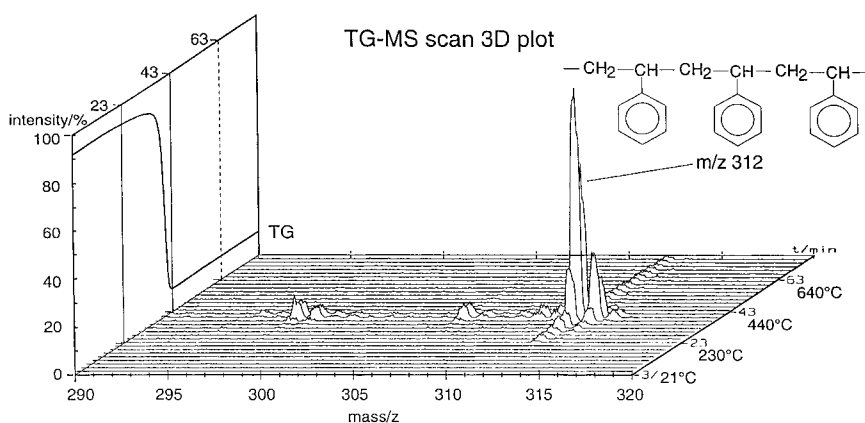
Fig. 8. Polystyrene decomposition measured with STA-MS Skimmer coupling, detection of tri-meric styrene fragment; 7.77 mg, helium 75 ml/min, 10 K/min.
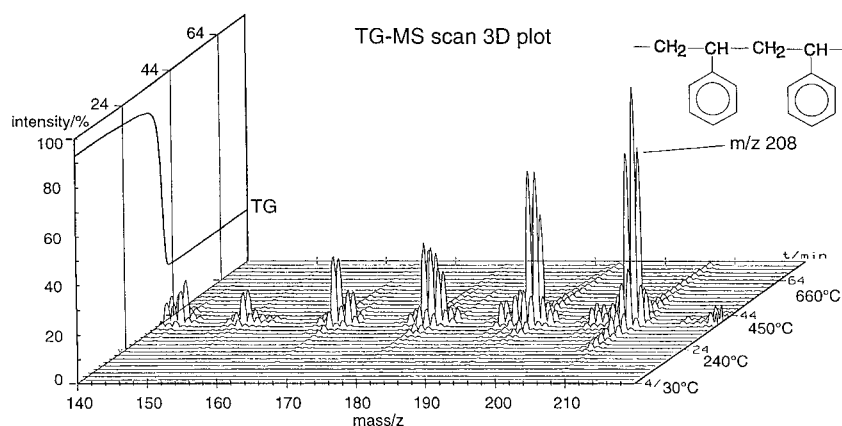

Fig. 9. Polystyrene decomposition measured with STA-MS Skimmer coupling system, detection of di-meric styrene fragment; 7.63 mg, helium 75 ml/min, 10 K/min.

The examples shown indicate the importance of continuous gas analysis to detect the gases evolved during the process. But the knowledge about gas evolution and the type of gas evolved is not sufficient for a fair estimation of an endangerment to the environment. The quantification of the individual species evolved must be of equally high priority. The pulse thermal analysis (PTA) technique was especially developed for a precise calibration of combined thermal analysis and gas-analysis techniques [5].

With the injection of known amounts of a calibration gas, one can get precise signals from the gas analyser, even on-line with an experiment running to detect evolved gases.

4. Summary

Many industrial production processes which apply heat to achieve the desired material properties, are accompanied by decomposition reactions and gas evolutions of varying degrees of importance. This has been shown for the firing of a traditional building material and for technical ceramics. It could also be transferred to the cement industry and, for a slightly different point of view, to power stations where energy is produced using fossil fuels. In polymer production and recycling processes, gases are to be expected in many cases. Only with precise qualitative analysis and quantitative detection of the evolved volatiles can

statements be made regarding the possible endangerment to the environment by these gaseous products. Thermal analysis is a versatile group of methods for the study of all these technical processes and, with combined gas-analysis methods, the necessary information on all volatile products can be obtained. A global kinetic analysis of reactions measured by thermal analysis can be the base for the prediction of long-term stability and decomposition behaviour.

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