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Comparative studies of polymers using TA–MS, macro TA–MS and TA–FTIR

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Abstract

The thermal degradation of polyamide 6, polyamide 66 and of polyamide 612 was studied using three different thermal analyzers with combined techniques for the evolved gas analysis (TA-MS and TA-FTIR). The sample masses were about 13 mg, 20 mg and 1 g; the heating rates were 2.6 and 10 K min^{-1}. Nitrogen, argon and synthetic air were used as carrier gases. The evolved gaseous products were captured on the resin XAD-4, desorbed and analyzed off-line by GC/MS. The advantages and limitations of each technique are emphasized as well as the form in which its application is maximized when using them simultaneously. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of new products in a responsible manner involves the critical examination of the *production cycle* from environmental and safety points of view. The *research* has to be done in such a way that provides information about the characteristics and structure of the materials, their possible risks and their spectrum of application. The *development* has to include the design of the product, process engineering, integrated environmental protection and has already to consider possible ways of disposal. The *production* itself must have an efficient management of energy and resources, has to count with safety procedures as well as with waste minimization measurements. The *retailing* must include safety data, low consuming packing and efficient transport. The *utilization* of the product has to be done in accordance to its safety data and only between its application ranges. The *recycling and disposal* have to consider the material or energetic recycling depending on its feasibility and on the resulting environmental impact.

Understanding the previous context, we can define several tasks within the study and investigation of the emissions being formed in incineration processes. The *objective* of such investigations can be defined as the study of the behavior of the substances during the combustion process. There are different *methods* to achieve this: to work with standard incineration ovens, to use thermal analysis, to utilize a pilot system or to use the data from an incineration plant. The *analytics and evaluation* of the samples must compile the physical–chemical characteristics (main component analysis, solubility in water, etc.), the ecological

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behavior (transport, accumulation, bio-availability) and their possible effects (acute and chronic toxicity, mutagenic and carcinogenic significance). The *consequences* of the studies have to include the avoiding and reduction of toxic products as well as the development of new products and production processes.

Within this framework, we focused our efforts in studying the thermal degradation of some polymers using two different coupled techniques: thermal analysis–mass spectrometry (TA–MS) and thermal analysis–Fourier transform infrared spectroscopy (TA–FTIR). These hyphenated techniques are a very useful tool in the investigation of the thermal decomposition and its mechanisms because they allow to have *simultaneous* information about the decomposition process itself and the evolving substances. TA–MS has been proved to be helpful in the understanding of thermal degradation [1–4]; TA–FTIR has also been proved as well to be useful as a coupled technique for the study of the thermal degradation [5–7]. The coupling of TA with MS and FTIR in one apparatus has also been reported [8].

In the present paper, we compare and describe in a practice form the thermal degradation of some plastics (polyamides) using three different thermal analyzers and emphasize their similarities and differences as well as their complementary application.

2. Experimental

The polymers used were polyamide 6 (PA 6), provided by Bayer AG (Durethan B30S), polyamide 66 (PA 66), provided by BASF AG (Ultramid A3) and polyamide 612 (PA 612), provided by Hüls AG (Vestamid D16nf).

The thermal degradation studies were performed on three different devices with coupled techniques for the evolved gas analysis (EGA). The first device consisted of a simultaneous thermal analyzer STA 429 (Netzsch Gerätebau GmbH) and an on-line coupled quadrupole mass spectrometer QMG 420 (Balzers Hochvakuum GmbH). The samples (ca. 20 mg) were heated from ambient temperature up to 800°C using a heating rate of 10 K min^{-1} in dynamic nitrogen and synthetic air conditions. The second device was a macro thermal analyzer STA 419 (Netzsch) with an on-line coupled quadrupole mass spectrometer QMG 421(Balzers). The rate of heating used was 2.6 K min^{-1} beginning from room temperature up to 800°C. Measurements were made using ca. 1 g samples in flowing argon and synthetic air atmospheres. The third device consisted of a thermobalance TG 209 (Netzsch) and an on-line coupled Fourier transform infrared spectrometer Vector 22 (Bruker Analytik GmbH). The samples (ca. 13 mg) were heated from ambient temperature up to 800°C with a heating rate of 10 K min^{-1} in dynamic nitrogen and synthetic air atmospheres.

Furthermore, the evolving gaseous products were adsorbed and enriched in the resin Amberlite XAD-4 in which desorption was done with acetone. The identification of the products was done off-line by GC/MSD, which consisted of a HP 6890 gas chromatograph and a HP 6890 mass selective detector. The operating conditions of the GC/MSD are described in Table 1.

Table 1
Operating conditions of the GC/MS (HP 6890)[a]

Oven ramp	Ramp rate (°C min^{-1})	Next (°C)	Holding time (min)
Ramp 1		40.00	2.00
Ramp 2	10	70.00	1.50
Ramp 3	3	90.00	0.00
Ramp 4	15	310.00	5.00

[a] Column: SGE BPX-5, 25 m, 0.25 mm i.d., 0.22 μm film. Injection: 2 μl splitless at 280°C. Transfer line: 300°C. Detector HP MSD 6890: 70 eV, SCAN modus. Solvent delay: 1.5 min. Carrier gas: helium with controlled constant flow of 1.5 ml min^{-1}.

3. Coupled techniques

The coupling of thermal analysis with gas analysis techniques provides a powerful analytical tool in which the advantage of each technique is enhanced by the other. Presented here is a brief description of the most common systems to couple thermal analysis with mass spectrometry and with Fourier transform infrared spectroscopy.

3.1. TA–MS couplings

The function of the TA–MS couplings is to allow the interaction between thermal analysis and mass spectrometry. Most of them can work in high vacuum and/or at normal pressure. There are three common TA–MS couplings: capillary; orifices and jet separators. The capillary coupling consists of one capillary that withdraws the gas from the hot zone of the furnace at a constant rate and conduces it into a second capillary with a by-pass inlet system where a small sample is taken into the mass spectrometer. The orifice coupling consists of a two-stage pressure reduction system that achieves the pressure needed for the operation of the mass spectrometer. The jet separator is based on the principle of molecular mass-dependent diffusion and consists of a capillary carrying the gases from the oven through a nozzle into a glass bulb and of a second capillary (aligned with the nozzle), which samples a fraction of the gas into the mass spectrometer.

The advantages of the capillary systems are the simple handling, the flexible application and their relatively low costs. The disadvantages are the partially condensation of the evolving gases, their naturally discrimination and the mechanical instability. The advantages of the orifice and jet separator systems are a minimum of condensation and that they do not decompose the gas stream. The disadvantages are the fixed assembly in the furnace and the relatively high price.

All the systems have to meet following requirements: representative sampling of the evolving products (avoiding separation and condensation), short response time (which ensures a real-time correlation of TA and MS data), high sensitivity and corrosion resistance.

3.2. TA–FTIR couplings

The TA–FTIR couplings usually work at normal pressure (but several can operate under vacuum) and can be internal or external. The core of the coupling is the transfer line, which consists of a heated tube or pipe that connects the TA apparatus to the infrared gas cell (which is heated as well). In this case the whole gas stream flows throughout the detector and not just a fraction of it.

The advantages of the transfer line are the simple handling, its flexible application and the relative low cost. The disadvantages are the eventual condensation and further decomposition of the gases. An advantage of the system is a vacuum tight gas cell. By evacuating the system, residual water can be excluded; after flooding with the desired gas, the atmosphere is well defined.

The requirements a TA–FTIR interface has to meet are the following: representative gas sampling; minimized dilution effects and low decomposition; short response time; high sensitivity; high resolution and corrosion resistance.

4. Results and discussion

The thermal degradation of aliphatic polyamides has been studied intensively in the past [1,6,9–11] because they are the most important group of the thermoplastic polycondensates. They show a similar behavior in their thermal degradation curves: they decompose in one step in inert atmospheres and in two steps in the case of synthetic air. The temperatures of the DTG peaks in nitrogen coincide with the temperatures of the first step in air. A very important factor affecting the degradation is the heating rate. Fig. 1 shows the TG curves of the thermal decomposition of PA 66 in air for the three thermal analyzers. The degradation rate is directly proportional to the heating rate, therefore the degradation rate is bigger in the case of the highest heating rates (10 K min^{-1}) but at the end all the measurements achieve the same weight loss (ca. 99%). At lower heating rates the degradation begins earlier but extends over a wider range of temperatures, which explains why the second step in air extends over a larger range of temperature in the case of the lowest heating rate (2.6 min^{-1}).

To illustrate the differences of the two TA–MS analyzers the thermal decomposition of PA 612 under synthetic air was chosen (Fig. 2). They do not only have different sample masses (20 mg vs. 1 g) but also a different transport of the reaction gas. In case of the STA 429 the gas flows from behind the crucible and surrounds it while in the case of the macro TA the gas is actively transported through the sample (which is embedded in a bed of inert material). The modification in design of the macro TA helps to avoid the formation of a micro atmosphere, which can lead to partially false results in the STA 429 analyzer (most of all when working with reactive atmospheres like air). The MS-spectra differ not just in intensity but also in the

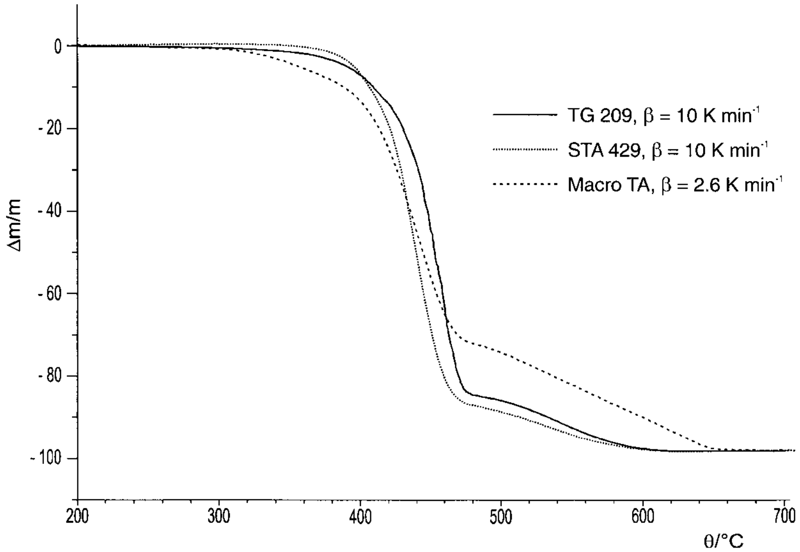

Fig. 1. TG curves of the thermal degradation of PA 66 in synthetic air.

pattern. The differences in the pattern are most probably due to the development of a micro atmosphere in the crucible, which leads to results more similar to those obtained under nitrogen for the STA 429. The products undergo a stronger reaction with the oxygen of the air in the case of the macro TA than in the case of the STA 429. The off-line analysis obtained by GC/MS allowed the main products of the thermal degradation (benzene, toluene, C_3–C_{11} nitriles, a C_6-lactam and 1,10-Dicyanodecane) to be identified and quantified.

Looking at the IR-spectra of the degradation of PA 6 in nitrogen and in air (Fig. 3) it is possible to identify all the functional groups typical of caprolactam (the

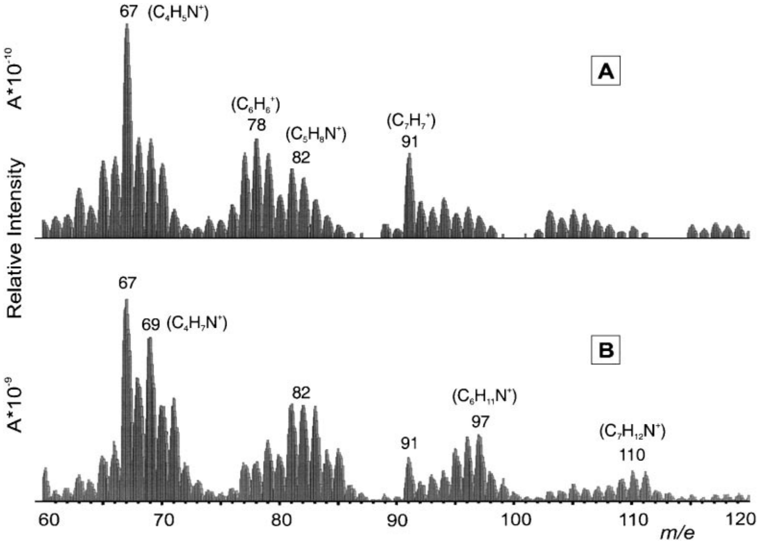

Fig. 2. MS-Spectra of the thermal degradation of PA 612 in synth. air on the a) Macro TA and b) STA 429.

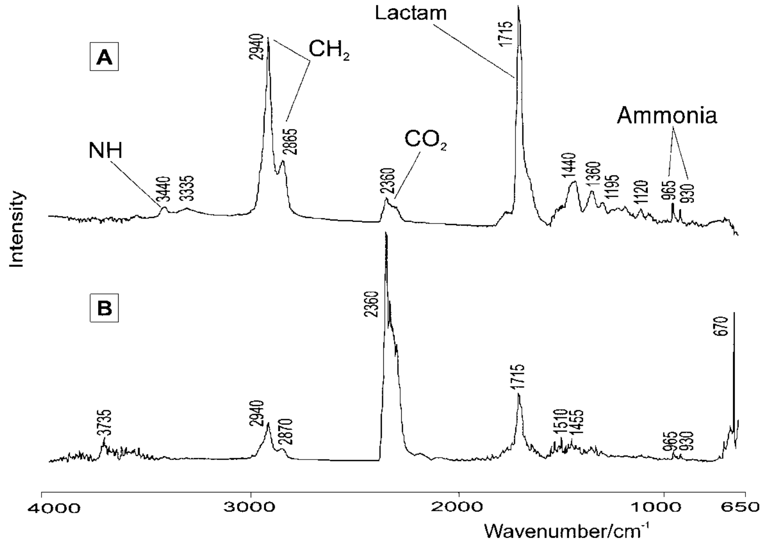

Fig. 3. IR-Spectra of the thermal degradation of PA 6 in a) nitrogen and b) synthetic air.

former monomer of PA 6): NH groups at 3440 cm^{-1}, lactam absorption at 1715 cm^{-1}, CH_2 groups at 2940, 2865 and 1440 cm^{-1} and absorptions in the fingerprint pattern at 1360, 1195 and 1120 cm^{-1}. In addition, it is possible to observe ammonia groups at 970 and 930 cm^{-1} in nitrogen. The intensities in nitrogen are higher than in air for all groups with exception of CO_2, which naturally increases in the degradation under air.

Examining also the degradation of PA 6 in both atmospheres with TA–MS (Fig. 4) it is possible to observe the ions corresponding to caprolactam: the ion intensity at $m/e=113$ (M^+), the main ion M^+ minus NH_3 and minus CO (or CH_2N) at $m/e=96$ and 85,

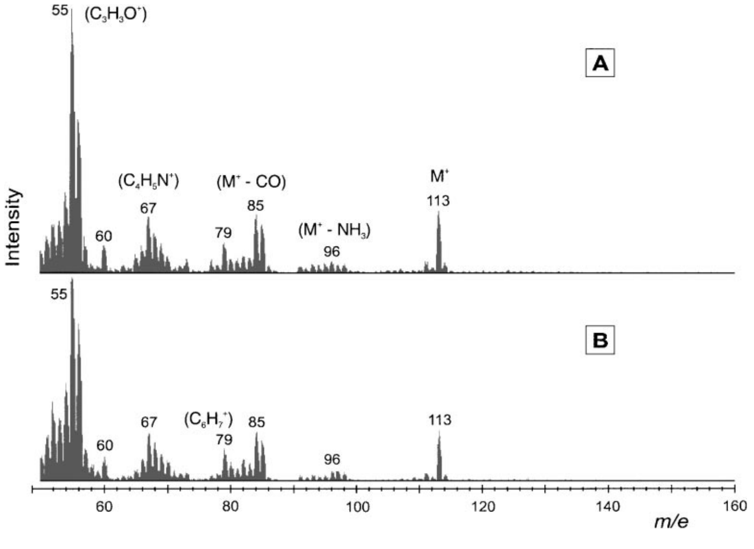

Fig. 4. MS-Spectra of the thermal degradation of PA 6 in the STA 429 for a) nitrogen and b) synthetic air.

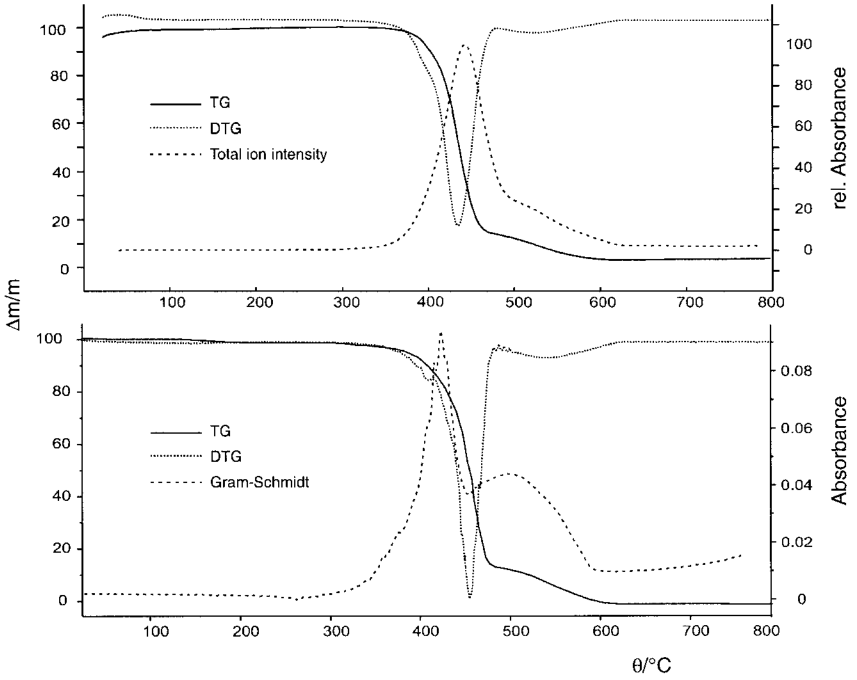

Fig. 5. TG, DTG, Integral ion spectrum and Gram-Schmidt curves of the thermal degradation of PA 66 in air.

respectively, $C_4H_5N^+$ at $m/e=67$ and $C_3H_3O^+$ at $m/e=55$. Furthermore, it is possible to identify another signal at $m/e=79$, which is likely to be ${C_6H_7}^+$ formed by condensation and further reaction of the amid groups. Both spectra show the same pattern in nitrogen and air, being the intensities higher in the case of nitrogen. A positive and final identification of the ions is just with the interpretation of the spectrum not achievable: in many cases there are several substances that could be assigned to the same ion signals and the only way to ensure an accurate identification is to perform further analysis with some other techniques (like FTIR or off-line with GC/MS).

Fig. 5 shows the total ion and the Gram–Schmidt curves of the degradation of PA 66 in air. The degradation is accomplished in two steps, being the second the smaller one. The second step is hardly to distinguish in the integral ion curve and looks like a small shoulder. For the contrary, in the Gram–Schmidt curve the second step is clearly visible and its maximum agrees with that of the DTG curve. This effect is explained studying the behavior of the different MS ion current intensity curves and the FTIR traces (Fig. 6). In MS it can be seen that NH_3 ($m/e=15$), H_2O ($m/e=18$) and HCN ($m/e=27$) evolve only during the first step, while CO_2 ($m/e=44$) evolves during both steps and is thus responsible for the second step. The contribution effect of the ion corresponding to CO_2 is strongly minimized in the total ion curve. Analyzing the FTIR traces the same behavior can be observed, being the trace of CO_2 (and of CO in a minor extend) the responsible for the second degradation step. The resulting Gram–Schmidt curve shows in a major extend the contribution of CO_2 because the intensity of its trace is very high compared to the other ones.

Finally, Fig. 7 shows at once three different spectra obtained from the degradation of PA 6 in nitrogen by the TA–MS and TA–FTIR analyzers. All spectra show the formation of caprolactam as the main product of the degradation of PA 6. The spectra of both TA–MS analyzers show the same pattern but different intensities, being greater in the case of the Macro TA. The functional groups are given by the IR spectrum and these results complement and reinforce the results obtained by TA–MS. The combination of both techniques makes easier the interpretation of the data and facilitates their correct identification and assignment.

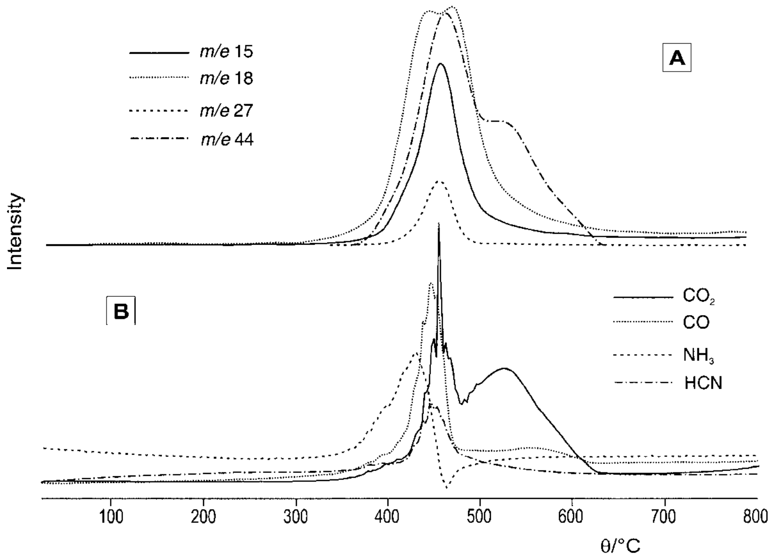

Fig. 6. Thermal degradation of PA 66 in synthetic air a) MS ion current intensity curves and b) FTIR trace curves.

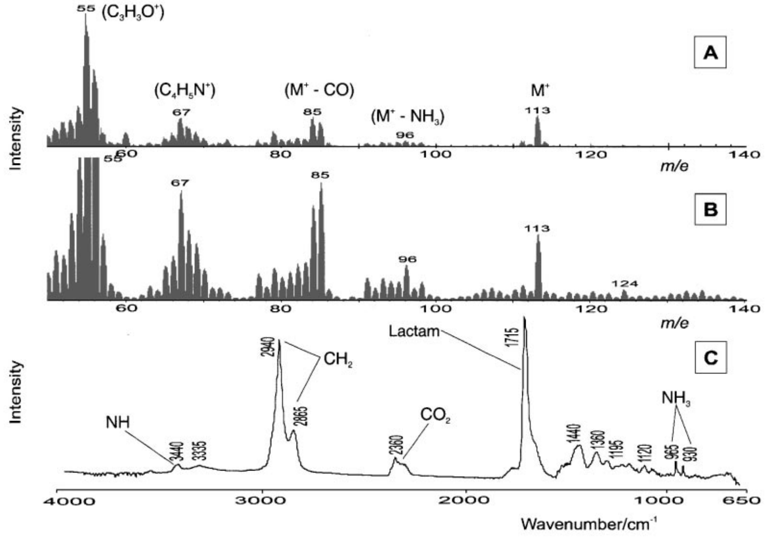

Fig. 7. Spectra of the thermal degradation of PA 6 in nitrogen for a) TA-MS 429, b) Macro TA-MS and c) TA-FTIR.

5. Conclusions

The performed studies on thermal degradation using the coupled techniques TA–MS and TA–FTIR appear to be helpful in the understanding and clarifying the decomposition process during polymer heating. Both techniques allowed the simultaneous (real-time) follow-up of different masses (*m*/*e* in MS) or of different functional groups (traces in FTIR) and of the TA data through the decomposition process. The information obtained from each technique separately was useful to establish possible degradation pathways and main products but it was not sufficiently strong to discern between products with similar characteristics.

Combining the results from both techniques it was possible to obtain information that single techniques alone would not provide. The presence of low concentration substances was achieved by off-line analysis with GC/MS. The studied techniques reinforce themselves mutually and can be applied in the investigation of the decomposition process of new substances or as a tool in the quality control of known substances. A complete study of the thermal degradation must include an off-line analysis to identify and quantify the low concentration products, which can possess high toxic potentials.

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