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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

THERMAL DEGRADATION STUDIES OF SOME ALIPHATIC POLYAMIDES USING HYPHENATED TECHNIQUES (TG-MS, TG-FTIR)

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Abstract

The thermal degradation of the aliphatic polyamides 6 and 66 was investigated by means of the combined techniques TA-MS and TA-FTIR. The analyses were performed in three different devices. Sample mass ranged from 13 mg to 1 g and heating rates of 2.6 and 10 K min^{-1} were used in both air and nitrogen atmospheres. The most important decomposition products were caprolactam for PA 6 and cyclopentanone for PA 66. Evolution of NH_3 and HCN was registered. The findings of the two hyphenated techniques led to the same results and complemented each other well. The evolved products were captured and analyzed off-line by GC/MS for further confirmation of results.

Keywords: polyamides, TA-FTIR, TA-MS, thermal degradation

Introduction

Plastics have made a decisive contribution to the present high living standard of the industrialized countries. Plastics based on natural products appeared first with vulcanized fibre in 1859 followed by celluloid and artificial horn in 1870 and 1897, respectively. The development of the thermosetting plastics commenced in the early part of the 20th century and the real breakthrough occurred with the polymerization of plastics in 1930 [1]. Polyamide 66 (PA 66) was first obtained in 1935 and polyamide 6 (PA 6) three years later in 1938 [2].

The most common method for the disposal of plastics is their incineration, which if not done appropriately can cause environmental problems, mostly due to the formation of toxic combustion byproducts. Incineration of plastics is carried out in a complex simultaneous combination of pyrolysis, gasification, ignition and combustion of pyrolysis products, accompanied by a transport of mass and energy. Thus it is important to study the pyrolysis and the combustion of the evolved pyrolysis products of plastics to attain an enhanced knowledge of the thermal degradation process and its mechanism, contributing to improve the incineration conditions and trying to minimize the risks for the environment.

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Polyamides (PA) are the most important and the most known group of the thermoplastic polycondensates. When they consist of one building block they are called polylactams (like PA 6, built from caprolactam) and if they are built of two main blocks they are called nylons (like PA 66, consisting of hexamethylenediamine and adipic acid). The thermal degradation of these polyamides has been studied systematically and intensively [3–9]. For PA 6 it has been reported that the main route of thermal decomposition is the production of the cyclic monomer (caprolactam) [3, 4]. Evolution of volatile gases like CO_2 and NH_3 has been also reported [5] as well as the presence of oligomeric products with nitrile and vinyl chain ends [5, 6]. PA 66 seems to have a peculiar decomposition mechanism which yields cyclopentanone as the main product [3, 6] but also a wide range of volatile and organic products like CO_2, H_2O, NH_3, cyclopentanone, hydrocarbons, dinitriles and cyclic monomer has been reported [7].

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. Thermal analysis – mass spectrometry (TA-MS) has been proved to be helpful in the understanding of thermal degradation [4, 10–12]. Thermal analysis – Fourier transform infrared spectrometry (TA-FTIR) is also an established technique for the study of the thermal degradation [13–14]. TA-FTIR studies on thermal decomposition of nylon 66 showed that NH_3 and CO were the main toxic gaseous products detected. H_2O and CO_2 were found as well [8].

Experimental

Polyamide 6 (PA 6) from Bayer AG (Durethan B30S) was a raw polymer without any additives. Polyamide 66 (PA 66) from BASF AG (Ultramid A3) was also a raw polymer without any additives. Both substances were in granulated form. 6-Caprolactam (>98%, Fluka Chemie, Switzerland), decanonitrile (for synthesis, Merck) and the rest of the alkanonitriles (>99%, Aldrich Chemie, Germany) were used as received. The structures of the polyamides investigated are shown in Table 1.

Table 1 Structure of the polyamides investigated

Trade name product(s)	Formula of repeat unit	Ratio CH_2:CONH	Former
Polyamide 6	$[–NH(CH_2)_5CO–]_n$	5	Caprolactam
Polyamide 66	$[–NH(CH_2)_6NHCO(CH_2)_4CO–]_n$	5	Hexamethylenediamine and Adipic acid

The studies of thermal degradation were performed using 3 different devices with hyphenated techniques. The first device consisted of a STA 429 simultaneous thermal analyzer (Netzsch Gerätebau GmbH) and an on-line coupled QMG 420 quadrupole mass spectrometer (Balzers Hochvakuum GmbH). The samples were heated from ambient temperature up to 800°C using a heating rate of 10 K min^{-1} in nitrogen and synthetic air atmospheres. The sample size used was about 20 mg. The second device was a STA 419 simultaneous thermal analyzer (Netzsch GmbH) with an on-line coupled QMG 421 quadrupole mass spectrometer (Balzers GmbH). The rate of heating used was 2.6 K min^{-1} beginning from room temperature up to 800°C. Measurements were made using about 1 g samples in flowing argon and air atmospheres. The third device consisted of a TG 209 thermobalance (Netzsch Gerätebau GmbH) and an on-line coupled Vector 22 Fourier transform infrared spectrometer (Bruker Analytik GmbH). The samples were heated from ambient temperature up to 800°C with a heating rate of 10 K min^{-1}. Air and nitrogen were used as atmospheres. The sample size used was about 13 mg.

The resin Amberlite XAD-4 was used for the enrichment and adsorption of the evolving degradation products, which desorption was done with acetone. After micro-filtration of the solution; the identification of the adsorbed products was done by GC/MS.

A HP 6890 gas chromatograph and a HP 6890 mass selective detector were used for the analysis of the degradation products. The GC was equipped with a SE-54 capillary column (Macherey-Nagel GmbH, 50 m, 0.35 mm i.d., 0.25 μm film); a HP 6890 automatic injector, injection volume=2 μl; splitless injection at 280°C; transfer line at 280°C; a temperature program starting isothermally at 40°C for 1 min; 40–60°C at 20 K min^{-1}; 2 min. Isothermal; 60–300°C at 10 K min^{-1}; 10 min. Isothermal; solvent delay 3.55 min; detector HP MSD 6890 (70 eV), modus SCAN. The carrier gas used was helium with a controlled flow of 1.6 ml min^{-1}.

Results and discussion

Both polyamides show a similar behavior in their thermal degradation curves. The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of PA 6 and PA 66 in nitrogen and in air atmospheres are shown in Figs 1 and 2 respectively. The TA data are listed in Table 2.

Table 2 TA data of PA 6 and PA 66

Polyamide	DTG maximum/°C	DTA maximum/°C	Δm/%
PA 6 in N_2	436	491	Δm_{tot}=95.8
PA 6 in air	423 525	– 531	89.8 7.4 Δm_{tot}=97.2
PA 66 in N_2	430	504	Δm_{tot}=94.5
PA 66 in air	434 524	443 523	86.2 10.8 Δm_{tot}=97

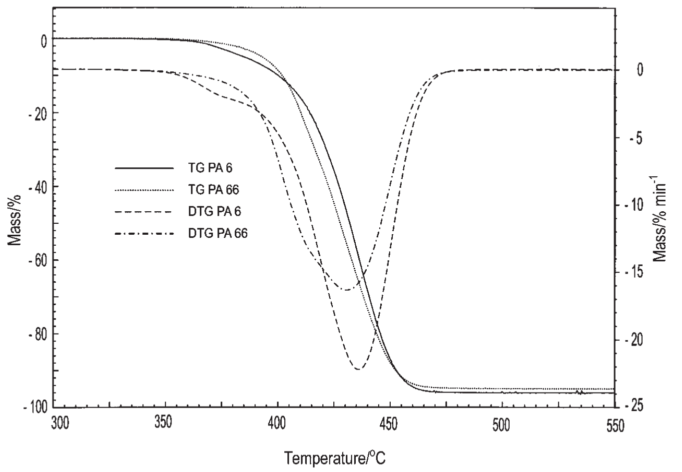

Fig. 1 TG and DTG curves of PA 6 and PA 66 in nitrogen atmosphere

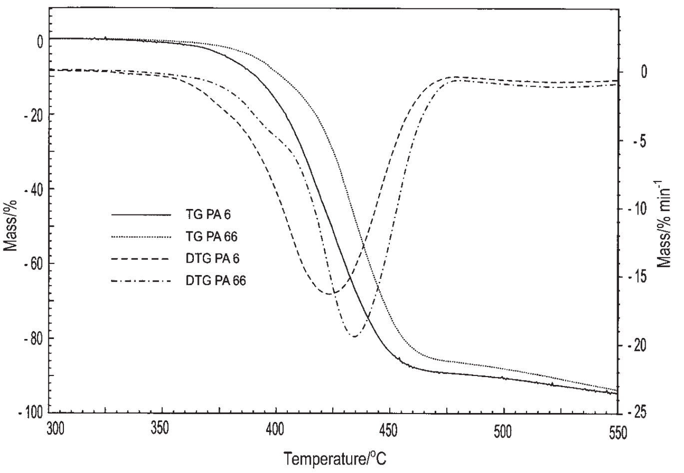

Fig. 2 TG and DTG curves of PA 6 and PA 66 in air atmosphere

Thermal degradation

Both polyamides decompose in nitrogen apparently in one step but the presence of a small shoulder at the beginning of the DTG curve indicates that at least two overlapping steps are occurring and are difficult to distinguish. Studies with lower heating rates confirmed this supposition and are in agreement with the literature [5, 7]. The mass loss takes place in the range of 350–475°C and the DTG curves show a maximum at 436°C for PA 6 and at 430°C for PA 66 (Figs 1 and 2).

The DTG curves in air show the occurrence of two decomposition steps with a dominant one at the beginning and a weak peak at higher temperatures. The first peak occurs in the same range of temperatures as the nitrogen peak but the DTG maxima are different. For PA 6 the DTG curve shows a maximum at 423°C and for PA 66 at 434°C. This peak also shows a small shoulder at its beginning and indicates once more that at least two overlapping steps are occurring in this temperature range. The second peak is weak and it takes place in the range 475–650°C, with a DTG maximum at 525 and at 524°C for PA 6 and PA 66 respectively. The concordance of the DTG maxima for the second step suggested a similar process to have taken place. The mass loss in air was greater than that in nitrogen by more than 1.5% for both polyamides.

GC/MS analysis

The analysis of the decomposition products adsorbed on XAD-4 via GC/MS showed that in the case of PA 6 the formation of caprolactam is the dominating mechanism in

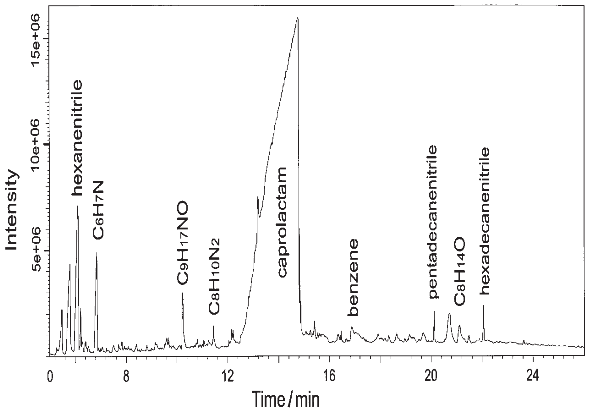

Fig. 3 Chromatogram of evolved products of PA 6 in nitrogen

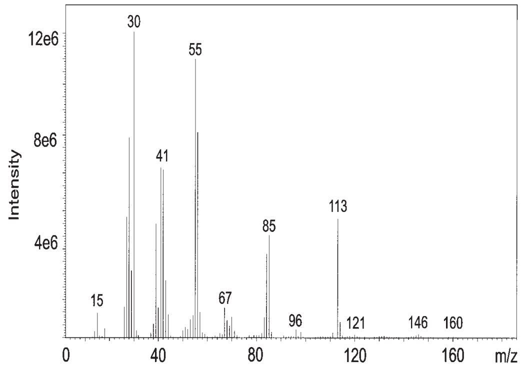

Fig. 4 Mass spectrum of caprolactam peak in Fig. 3

both atmospheres, nitrogen and air, but in nitrogen its formation is favored because of the lack of oxygen to oxidize it. In air the intensity of the caprolactam peak is much weaker than in nitrogen and pentanone and different aliphatic nitriles were also found to be present. Figures 3 and 4 show the chromatogram of the evolved products from PA 6 in nitrogen and the mass spectrum for the peak of caprolactam, respectively.

The GC/MS analysis for the evolved products from PA 66 in nitrogen showed only a few substances consisting mainly of cyclopentanone, a couple of dinitriles and cyclic monomer. The analysis for the products from PA 66 in air showed the presence of two relevant peaks, hexanedinitrile and cyclopentanone, as well as two small peaks of hexanenitrile and cyclic monomer.

TA-MS analysis

The use of the hyphenated technique TA-MS allows the collection of information about the evolution of the main products throughout the whole process of degradation. In the SCAN modus it is possible to select a range of masses to be detected and in the SIM modus it is possible to specify certain masses to be searched for.

The mass spectrum taken at the DTG maximum of the thermal degradation of PA 6 in both atmospheres and in both TA-MS devices registered intense signals at m/z 30, 41, 55, 67, 85, 96 and 113. The signal was more intense in the STA 419 than in the STA 429 not only because of the greater amount of the sample (1 g *vs*. 20 mg), but because of the active carrier gas transport flowing through the crucible, which eliminated the possibility of the formation of a micro-atmosphere consisting of a mix of evolved gases and carrier gas. Figure 5 shows the mass spectrum for PA 6 in both devices at DTG maximum and nitrogen atmosphere. It can also be seen that the main registered signals correspond to the mass spectrum of the caprolactam peak (Fig. 4) obtained with the off-line determination made by GC/MS. For PA 66 intensive signals at m/z 41, 55, 67 and 84 could be registered in both atmospheres. The signals

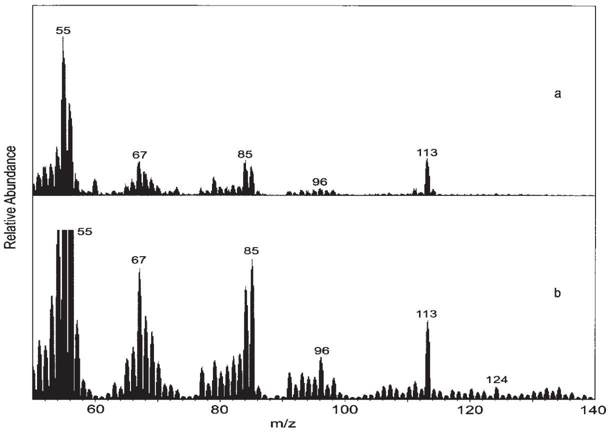

Fig. 5 Mass spectrum of PA 6 at DTG_{max} in the a – STA 429 and b – STA 419 TA-MS devices

from the STA 419 were also here more intense than from the STA 429. As in the case of PA 6, the occurrence of the main signals could be related to the formation of the most important evolved product, which in this case is cyclopentanone. This could be confirmed by means of comparing the obtained spectrum with a standard one.

TA-MS makes it possible to generate ion curves along the whole or just a partial range of the thermal degradation. MS ion curves of NH_3 and HCN were generated for PA 6 and PA 66 in nitrogen and in air (Fig. 6). The curve corresponding to NH_3 is in all cases more intensive than the one corresponding to HCN. Furthermore, the formation of both NH_3 and HCN is greater for PA 66 than for PA 6. This seems to be in contradiction to the expected values looking only at the ratio CH_2:CONH for both polyamides (Table 1). Taking the structures of the main degradation products into account an explanation for this fact is found. In contrast to caprolactam, cyclopentanone has no nitrogen in its structure, leaving consequently more nitrogen disposable for the formation of N-containing species.

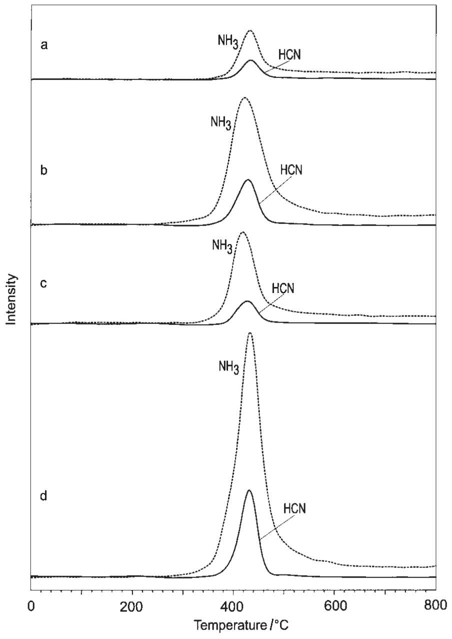

Fig. 6 MS ion current intensity curves of NH_3 at *m/z* 16 and HCN at *m/z* 27 for both polyamides: a – PA 6 in nitrogen; b – PA 6 in air; c – PA 66 in nitrogen; d – PA 66 in

Analyzing the MS ion curves of carbon dioxide at m/z 44 for all the samples, it could be seen that this is the product responsible for the second degradation step observed in the DTG curves of both polyamides in air. Because no other ion curves showed this behavior, it could be concluded that char is formed in the first degradation step and it undergoes combustion in the second step, which also leads to a higher mass loss in air (Table 2).

TA-FTIR analysis

The hyphenated technique TA-FTIR makes it possible to obtain the IR spectra from the evolved products of the degradation process. This is achieved applying the Fourier Transform technique to the measured interferograms. It is possible to select a wavenumber range and define a trace to be trailed through the whole process.

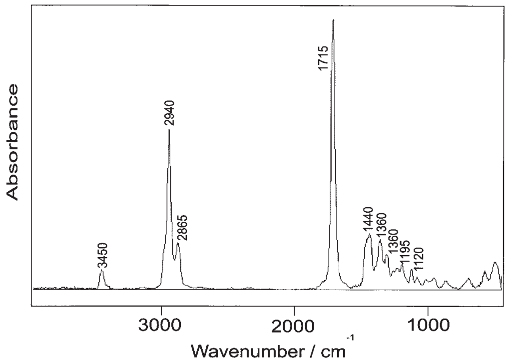

Fig. 7 Infrared spectrum of caprolactam

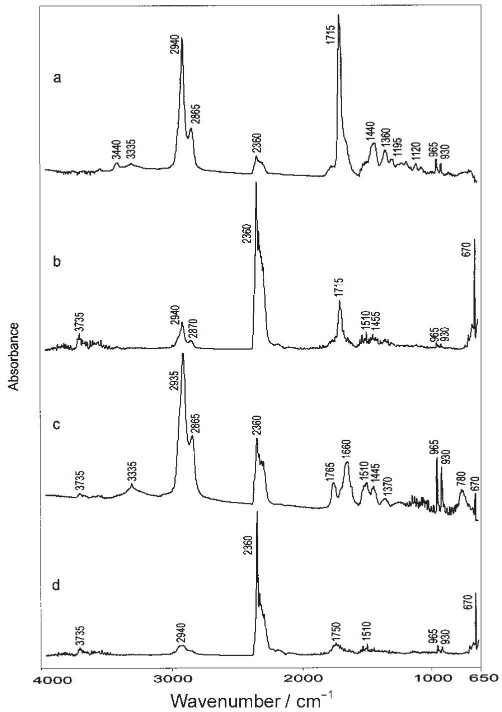

Fig. 8 Infrared spectra at DTG_{max} of: a – PA 6 in nitrogen; b – PA 6 in air; c – PA 66 in nitrogen; d – PA 66 in air

The spectrum from PA 6 in nitrogen shows all the IR absorptions typical of caprolactam (Fig. 7), the main evolved product, as can be seen in Fig. 8(a): NH groups at 3440 cm^{-1}, CH_2 groups at 2940, 2865, 1440 cm^{-1}, lactam absorption at 1715 cm^{-1} and the fingerprint pattern in the region 1360–1120 cm^{-1}. However, products absorbing at 2360 cm^{-1} (CO_2) and at 965 and 930 cm^{-1} (NH_3) are also present. The spectrum in air (Fig. 8(b)) is similar but in this case the absorption of CO_2 at 2360 and 670 cm^{-1} dominates over the others. The spectrum from PA 66 in nitrogen (Fig. 8(c)) shows, in contrast to PA 6, a considerable amount of evolving CO_2 (2360 and 670 cm^{-1}). Following absorptions were also found: NH groups at 3440 cm^{-1}, CH_2 groups at 2935, 2865 and 1445 cm^{-1}, amide (1660 cm^{-1}), carbonyl at 1765 cm^{-1}, NH_3 at 965 and 930 cm^{-1}. The mentioned absorptions correspond to the main formed products cyclopentanone and dinitriles. As in the case of PA 6 the spectrum of PA 66 in air (Fig. 8(d)) shows a considerable peak of CO_2 and small amounts of the other substances.

Analogous to the TA-MS procedure traces for NH_3 (930 cm^{-1}) and HCN (712 cm^{-1}) were generated for both polyamides in nitrogen and in air (Fig. 9). The intensity of NH_3 is here in all curves substantially larger than the intensity from HCN. As observed in the TA-MS analysis the development of NH_3 and HCN is as twice as big in the case of PA 66 compared to PA 6. The peak's maximum for all the NH_3 curves seems to be in the same temperature range but in the case of HCN it seems to vary. In the case of PA 66 in air (Fig. 9(d)), it occurs earlier than in the other cases. This effect may arise from an interfer-

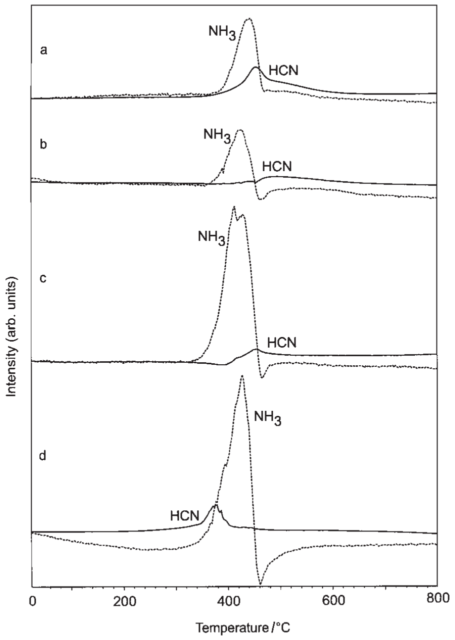

Fig 9 IR trace curves of NH_3 and HCN for both polyamides: a – PA 6 in nitrogen; b – PA 6 in air; c – PA 66 in nitrogen; d – PA 66 in air

ence of other bands with the nitrile group. This effect can also be responsible for the apparent high evolution of HCN in the TA-MS curves.

CO_2 traces in air showed two degradation steps and confirmed the formation of char in the first degradation step of the DTG curve and its corresponding pyrolysis in the second step. CO traces showed no development in nitrogen and a two step curve in air, which reinforced the assumption based on the CO_2 found.

Conclusions

The studies performed on the thermal degradation of PA 6 and PA 66 by TA-MS and TA-FTIR show that these hyphenated techniques are helpful to clarify the process of degradation and the evolution of the main evolved products. Both techniques allow the follow up of different ions (MS) or traces (FTIR) through the whole degradation process, which together with the TA data, permit the establishment of the main degradation pathway. For PA 6 it was found that the main degradation product is caprolactam and for PA 66 it was cyclopentanone and ammonia. The formation of NH_3 was found to be larger than that of HCN. CO_2 and CO were found to be responsible for the second degradation step in air. The results obtained from each technique helped to reinforced the founds reciprocally. However, an identification of all the evolved products was only possible by means of the GC/MS off-line analysis, which allowed the further classification of the degradation products.

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