



# Thermal extraction combined with thermal desorption: A powerful tool to investigate the thermo-oxidative degradation of polyamide 66 materials



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## ABSTRACT

Using thermogravimetric analysis (TGA) with a solid-phase adsorber for thermal extraction, followed by subsequently analysing the adsorber with thermo-desorption gas chromatography mass spectrometry (TDS-GC-MS) enables measurement of polymer degradation under oxidizing atmosphere, and the identification of certain complex hydrocarbon degradation products by chromatographic separation and defined mass patterns. This technique, thermal-extraction desorption gas chromatography mass spectrometry (TED-GC-MS) was used to investigate the thermo-oxidative degradation of PA 66 and PA 66 doped with 2 wt% of metal oxide particles. In TGA pure PA 66 formed more residue under an oxidizing atmosphere than an inert one. In contrast to the measurements under inert atmosphere, several condensed aromatic species containing nitrogen could be identified in thermo-oxidative measurements. These degradation products were formed through condensation reactions of primary amides originating from imide hydrolysis. The formation of such highly condensed species also causes higher char formation. Four metal oxides have shown an impact on the thermo-oxidative degradation of PA 66:  $\text{Fe}_2\text{O}_3$  on  $\eta\text{-Al}_2\text{O}_3$  < pure  $\text{Fe}_2\text{O}_3$  =  $\text{Fe}_2\text{O}_3$  on  $\gamma\text{-Al}_2\text{O}_3$  < pure ZnO. For ZnO even a char-stabilizing effect could be observed. A catalytic effect of these metal oxides causes more condensed cyclopentanone and pyridine derivatives. Thus, more water is formed and released, resulting in increased hydrolysis of the imides and degradation at lower temperatures.

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## 1. Introduction

Polymers are becoming more and more important because of their low cost, their flexible processing and forming possibilities and their diverse material characteristics. These include, for example, broad variation in mechanical characteristics (stiffness and elasticity), special functionalities for electronic and optic applications and advantages in saving weight, especially in composite materials. Unfortunately, all polymers degrade, especially at elevated temperature and undergo reactions with oxygen [1]. These reactions restrict the application of polymers in areas of high temperature (exhaust heat of electric devices or in tribology) and for long-term applications. Although several functional solutions exist to protect polymers against this degradation (e.g. antioxidants, flame retardants), detailed knowledge about the molecular

decomposition mechanism for polymers depending on the atmosphere (with and without oxygen) is often lacking.

For polyamides, for example, an oxidizing atmosphere in combination with an increase in temperature is enough to yield visible changes (yellowing) in the polymer matrix, caused by the formation of crotonized aldehydic groups [2] or pyrrole [3] species. Therefore, special treatments like an inert atmosphere are necessary for processing polyamides [4]. A major challenge in the area of fire retardancy is to protect polymers against ignition, which is caused by a complex action of polymer pyrolysis and temperature, but also the amount of available oxygen. Hence, thermal and thermo-oxidative processes have to be considered. Furthermore, it is known that metal ions catalyze the decomposition of peroxides in polymers and thus influence oxidative degradation [5]. On the other hand, direct contact between metal and a polymer can induce the decomposition of polymer, commonly known as metal-induced decomposition (MID) [6].

To investigate the decomposition mechanism, thermo-analytical methods like thermogravimetry (TGA) coupled with

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infrared spectroscopy [7–9] (FTIR) or mass spectrometry [10,11] (MS) are commonly used. When measurements in TGA-FTIR/MS are performed under oxygen, often only signals of total oxidation products (water, carbon dioxide, carbon monoxide) can be observed, because the transfer from TGA to the gas analysis cell requires a distinct time, during which hydrocarbon decomposition products can oxidize further. As a consequence, the gas analysis of these methods detects a combination of solid-phase oxidation at the sample surface and gas-phase oxidation in the transfer line to FTIR. Therefore, very often no useful conclusions can be drawn from these measurements.

Complex hydrocarbons can generally be identified very easily using databases in chromatographic methods. Very common for polymers is pyrolysis gas chromatography mass spectrometry (Py-GC-MS) [12,13], but with most systems it is not possible to measure in an oxidizing atmosphere due to the protection of the MS system. However, various works have been published on oxidative measurements under moderate temperature conditions. Gröning et al. carried out thermo-oxidative long-term degradation studies of the gas phase with headspace solid-phase microextraction gas chromatography mass spectrometry (HS-SPME-GC-MS) for ambient temperatures up to 100 °C [14–16]. White et al. carried out their thermo-oxidative investigations with a cryo-GC/MS and stresses polyamide up to 138 °C [17–20].

In the present work we investigate the molecular, thermo-oxidative decomposition mechanism of polymers with a new method, thermal extraction and desorption coupled with gas chromatography mass spectrometry (TED-GC-MS) [7], which enable the improved detection of decomposition products under nitrogen [21] but also under an oxidizing atmosphere. In contrast to Gröning and White, we are able to investigate the gas phase of polymers up to complete thermo-oxidative decomposition (600 °C). This method combines the advantages of TGA (thermal, thermal-oxidative measurements) with the advantages of a chromatographic system that can separate the degradation products and subsequently identify with a high molecular resolution due to MS spectra. This was solved by thermal extraction of the decomposition products from the TGA on twistlers. These twistlers are small stir bars with an adsorption material (polydimethylsiloxane, PDMS) on the surface, which were developed for liquid analysis [22] (stir bar sorptive extraction, SBSE). Due to their defined adsorption surface and adsorption capacity, semi-quantitative [21] and even quantitative measurements can be carried out.

The polymer we chose for the investigation was polyamide 66 (PA 66), which is a widely used polymer, also known as nylon 66. Many investigations of the thermal degradation behaviour of PA 66 up to high temperatures, including evolved gas analysis, can be found in the literature [23–28]. However, due to the difficulties of measuring under air as mentioned before, there are fewer and less satisfactory investigations [10,29] of thermo-oxidative degradation behaviour with evolved gas analysis and temperatures up to 600 °C.

It is known that metal oxides [30–32] and salts [33–38] can have an influence on the polymer matrix of polyamides. This can lead to better thermo-oxidative stability due to complex redox chemistry and radical scavenging [31,35,39]. Therefore, we modified the polyamide material with 2 wt% of several metal oxides, in order to investigate the influence of various ions on the thermo-oxidative decomposition of PA 66. The influence of metal oxides on the thermal decomposition behaviour of PA 66 is presented in the former work [21]. The present paper presents – together with the former article about the thermal decomposition of PA 66 – a comprehensive work about the molecular decomposition schemes of polyamide 66 and polyamide 66, doped with metal ions. Detailed decomposition schemes were presented and the results reflect the advantages of the new method and analyze in detail the influence of metal ions on the material decomposition.

**Table 1**  
Summary of parameters for the TED-GC-MS measurements.

Parameter	Value	Parameter	Value
<b>Thermal desorption system (TDS)</b>		<b>Gas chromatograph (GC)</b>	
Initial temperature/°C	25	Flow/mL min <sup>-1</sup>	1
Heating rate/°C min <sup>-1</sup>	40	Start temperature/°C	40
End temperature/°C	200	Heating rate/°C min <sup>-1</sup>	5
Transfer line temperature/°C	250	End temperature/°C	300
<b>Cooling injection system (CIS)</b>		<b>Mass spectrometry (MS)</b>	
Initial temperature/°C	-100	Hold time/min	3
Heating rate/°C s <sup>-1</sup>	12	<b>Mass</b>	
End temperature/°C	270	Scan range/m/z	30–350
		Temperature quadrupole/°C	150
		Temperature ion source/°C	230

## 2. Experimental

### 2.1. Materials

The polyamide 6,6 (Ultradid<sup>®</sup>, PA 66) powder and the metal oxide-doped polyamide powders were provided by the BASF. As metal oxides Fe<sub>2</sub>O<sub>3</sub>, ZnO,  $\gamma$ - and  $\eta$ -Al<sub>2</sub>O<sub>3</sub> as well as Fe<sub>2</sub>O<sub>3</sub> on  $\gamma$ - and  $\eta$ -Al<sub>2</sub>O<sub>3</sub> carrier particles were used. All polymer samples were doped with 2 wt%. The amount of doping on the carrier particles ( $\gamma$ - and  $\eta$ -Al<sub>2</sub>O<sub>3</sub>) was 5 wt%. This results in a doping of 0.1 wt% of Fe<sub>2</sub>O<sub>3</sub> in the polymer matrix. The particle size distribution was controlled by scanning electron microscopy and showed a homogenous distribution of particles in the polymer, but also a broad distribution of particle size (about 30–130  $\mu$ m). GPC and DSC measurements were carried out to verify that the production process of these materials did not significantly degrade the polymer matrix

### 2.2. Methods

Polymer sample masses of 2.00 ± 0.02 mg were weighed in aluminium oxide pans and used for thermal extraction in TGA (TGA/SDTA 851, Mettler/Toledo, Gießen, Germany). They were heated from 25 to 600 °C at a heating rate of 10 °C min<sup>-1</sup>. As the purge gas, nitrogen or synthetic air with a flow rate of 30 mL min<sup>-1</sup> was chosen. The twistlers were fixed in the thermal desorption glass tube with two stainless sieves and coupled to the outlet of the TGA with a self-built interface.

A TDS-A2 sampler (Gerstel, Mülheim a/d Ruhr, Germany) was used for thermal desorption. It was mounted on a cooled injection system (CIS) with a glass-wool-filled glass liner. The GC-MS system (6890+ GC, MSD 5973N) was from Agilent (Agilent Technologies, Palo Alto, CA, USA). A HP-1MS (length 30.0 m × diameter 250  $\mu$ m × film thickness 0.25  $\mu$ m) column was used for all measurements. Helium was used for desorption and as the carrier gas for the GC. The compounds were identified by scanning the NIST 11 and Wiley 9th spectral databases. A summary of all necessary parameters is presented in Table 1. The twistlers could be reused. They were cleaned with 10 mL methanol for 10 min in an ultrasonic bath and baked for 50 min in a TC 2 tube conditioner (Gerstel, Mülheim a/d Ruhr, Germany) at 200 °C with a nitrogen purge gas flow of 60 mL min<sup>-1</sup>. A detailed description of this method can be seen elsewhere [7].

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