



Thermal decomposition studies of bio-resourced polyamides by thermogravimetry and evolved gas analysis



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ABSTRACT

In this work the degradation process of polyamides (PAs) based on renewable resources – PA 4.10, PA 6.10, PA 10.10 and PA 10.12, was studied by thermogravimetry (TG) coupled with evolved gas analysis (EGA) by infrared spectrophotometry (IR), quadrupole mass spectrometry (QMS).

The TG/FTIR/QMS studies in inert atmosphere showed that the thermal decomposition of bio-polyamides takes place with the evolution of alkenes, nitriles, cyclic species and low molecular weight compounds – carbon monoxide, carbon dioxide, water and ammonia. The thermo-oxidative decomposition of bio-polyamides start with *N*-vicinal methylene group and follow with the scission of alkyl-amide or vicinal C–C bond. The high energy reactions result in production of mainly low molecular gases (CO₂, CO, H₂O, NH₃). Char residue analysis revealed the presence of carboxylic end groups, which may participate in secondary reactions during degradation, resulting in crosslinks, and decomposing to carbon dioxide. Taking into account the thermoanalytical results obtained, the thermal decomposition pathway for bio-polyamides in inert atmosphere has been postulated.

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1. Introduction

Bio-resourced polyamides are ‘green’ polymers synthesized from castor oil derivatives and as engineering polymers display advantageous mechanical properties, such as high toughness, hardness, and abrasion resistance. Natural oils, replacing petroleum-based ones, are good alternative feedstock in the ‘green chemistry’ approach and have received an increasing attention in the last decade [1–5]. Bio-polyamides from renewable resources link typical long-chain polyamide properties, such as low moisture absorption, with high melting point and high crystallization rate [6–8]. However, their thermal stability which is crucial for processing purposes and may limit novel applications, has not been investigated in detail so far.

The mechanism of thermal decomposition of aliphatic polyamides was studied already in 1960s by Madorsky [9], and then by the other authors [10–12]. A series of compounds –

hydrocarbons, nitrogen containing species and low molecular gases CO₂, CO, H₂O, NH₃ and HCN have been identified in volatiles emitted during decomposition of polyamides. Besides, it has been found that poly lactams like PA 6, PA 12 decompose to the monomeric or oligomeric cyclic products, and diamino-diacid based polyamides (PA 6.6, PA 6.10, PA 6.12) produce usually linear and cyclic oligomeric compounds and monomeric units. The thermal degradation starts from homolytic scission of the *N*-alkylamide or peptide C(O)–NH bonds and can compete with other mechanisms, depending on experimental conditions, such as water presence or gas atmosphere. In general, at the beginning primary reactions of scission take place and the decomposition products can further degrade to produce various hydrocarbon fragments of lower molecular mass, while secondary reactions lead to light volatile gases and cross-linked fragments.

Thermogravimetric analysis (TG) coupled to Fourier-transform infrared spectroscopy (FTIR) and/or quadrupole mass spectrometry (QMS) is one of the most useful methods for investigating the thermal degradation of polymeric materials. The coupled methods allow simultaneously not only to characterize the thermal

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behavior of the material, but also to identify on-line volatile components released during the measurement and thus to get an insight into the mechanism of decomposition. Studies on the thermal degradation of polyamides using TG couplings with IR, QMS, and GC/MS helped to understand their decomposition behavior and to postulate stabilization actions [11–15].

In this work the thermal decomposition of bio-polyamides in inert and oxidative atmospheres is reported for the first time, including identification of the evolved gaseous products by hyphenated techniques and characterization of the solid residue after decomposition.

2. Experimental

2.1. Materials

Polyamides used in this study were bio-resourced products of DSM (PA 4.10–EcoPaXX[®] Q170MS) and Evonik (PA 6.10, PA 10.10, PA 10.12–VESTAMID[®] Terra) with specification presented in Table 1. All materials were used as received.

2.2. Testing methods

2.2.1. Thermogravimetry (TG)

Thermal degradation of bio-PAs was studied in air and argon atmosphere using a Netzsch TG 209 thermogravimetric analyzer. The sample of about 5 mg was placed in aluminum oxide crucible and heated at 10 deg/min from room temperature to 600 °C.

The solid residue taken at temperature of the DTG maximum (in air) was characterized by FTIR (PerkinElmer Spectrum 65 spectrophotometer, ATR mode, 8 scans, 4 cm⁻¹ resolution).

2.2.2. Evolved gas analysis (TG/FTIR/QMS)

The course of bio-polyamides degradation was investigated by TG/FTIR/QMS coupled method in inert (helium) and oxidative (air) atmosphere. The TG measurements were carried using a STA 449 Jupiter F1 instrument (Netzsch, Germany) under following conditions: heating rate of 10 deg/min, gas flow (helium 50 ml/min, air 50 ml/min), temperature range of 25–600 °C, sample mass ca. 20 mg. The volatile products evolved during heating were detected by FT-IR spectrophotometer Bruker (TENSOR27) and mass spectrometer QMS 403C Aëolos coupled on-line to the STA instrument. The gas cell of FTIR spectrometer and connecting tube were maintained at 200 °C. The spectra were recorded in the spectral range of 650–4000 cm⁻¹ with 16 scans per spectrum at a resolution of 4 cm⁻¹. The QMS was operated with an electron impact ionizer with energy of 70 eV. During the measurements *m/z* ratio was recorded in the range 10–150 amu, where *m* is the mass of molecule and *z* is its charge.

The evolved gaseous mixtures were analyzed using reference spectra of chemicals available in the instrument database (EPA Vapor Phase Library), and in the NIST database [16].

3. Results and discussion

3.1. Thermal degradation studies

From the TG/DTG profiles (Figs. 1 and 2) the onset temperature (*T*₀), the temperature corresponding to the maximum mass loss rate (*T*_{DTG}), mass loss at different stage of degradation, and char residue were determined – Table 2.

Polyamides present one step mass loss during degradation in inert atmosphere, while the oxidative environment influences the decomposition mechanism toward a multi-step process – Figs. 1 and 2.

There are no major differences in the thermal behavior of bio-based polyamides in inert atmosphere – materials start to decompose at ca. 440 °C with one weight loss step in the temperature range of 440–500 °C. The highest temperature of the maximum decomposition rate was found for polyamide 4.10.

In the oxidative measurements, one can observe that bio-polyamides differ in their thermal stability according to the amine segment length in the macrochain. The initial mass loss for polyamides with shorter amine blocks (PA 4.10, PA 6.10) was found at 369 °C with 3 wt.% mass loss (Fig. 2), whereby the polyamides 10.10 and 10.12 start to decompose at 401 and 410 °C, respectively. The main decomposition step occurs in the temperature range of 400–500 °C, followed by a small weight loss in the higher temperature range of 500–600 °C.

Analysis of the DTG profiles reveals that the decomposition process involves few overlapping steps indicating a complex degradation pathway.

The char residue at 600 °C in air was ca. 1.2 %, while in argon from 0.44 for PA 4.10–4.05 for PA 6.10. Based on the TG results, one can suggest that in the first decomposition step water and low molecular weight products are volatilized, following the main chain degradation and formation of solid residue through cross-linking and cyclization reactions [17].

The solid residue of the thermal decomposition of bio-polyamides in air taken at *T*_{DTGmax} was analyzed by FTIR (Fig. 3).

On the spectra of PA 6.6 vibration bands at about 936 and 906 cm⁻¹ were assigned as markers of polyamide crystallinity [18], and their intensity was considered as a measure of polyamide crystallinity [19–21]. Analogous peaks are observed in the spectra of all homologous polyamides. Interestingly, the band at ca. 940 cm⁻¹ for PA 10.10 is also visible after the first stage of degradation at 346 °C (Fig. 3), indicating that crystalline structure was basically preserved up to this temperature. However, in the spectrum of PA 10.10 residue, that was heated up to the *T*_{max} of the second degradation step, the absorption bands considered as crystalline markers disappear. This is an indication that the polyamide structure reached high degree of disorder as a result of growing number of different functional groups, including end groups. In addition to a former observations the significant increase of relative intensity of N–H stretching vibrations band at about 3300 cm⁻¹ in relation to stretching vibrations band of C–H bonding with maximum at 2923 cm⁻¹ suggests that amine end group concentration increases

Table 1
Specification bio-polyamides in the course of this work.

Bio-PA	Repeating unit	Based on	
		Acid	Amine
PA 4.10	[–NH(CH ₂) ₄ NHCO(CH ₂) ₈ CO–]	1,10-Decanedioic (sebacic)	1,4-Butane
PA 6.10	[–NH(CH ₂) ₆ NHCO(CH ₂) ₈ CO–]		1,6-Hexamethylene
PA 10.10	[–NH(CH ₂) ₁₀ NHCO(CH ₂) ₈ CO–]		1,10-Decamethylene
PA 10.12	[–NH(CH ₂) ₁₀ NHCO(CH ₂) ₁₀ CO–]	1,12-Dodecanedioic	1,10-Decamethylene

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