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Thermal Degradation of Poly(ε-caprolactone), Poly(L-lactic acid) and their Blends with Poly(3-hydroxy-butyrate) Studied by TGA/FT-IR Spectroscopy

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Summary: The thermal degradation behavior of poly(ε-caprolactone) (PCL) and poly(L-lactic acid) (PLA) have been studied in different environment. It was found that these polymers undergo completely different degradation processes in nitrogen and oxygen atmosphere. In oxygen environment PCL and PLA mainly decompose to CO_2, CO, water and short-chain acids. In nitrogen atmosphere PCL releases 5-hexenioc acid, CO_2, CO and ε-caprolactone, whereas PLA decomposes to acetaldehyde, CO_2, CO and lactide. The polymer blends of poly(3-hydroxybutyrate) (PHB) with PCL and PLA decompose similar to the individual homopolymers with crotonic acid as the initial decomposition product of PHB.

Keywords: poly(ε-caprolactone) (PCL); poly(3-hydroxybutyrate) (PHB); poly(L-lactic acid) (PLA); thermal degradation; thermogravimetric analysis (TGA)/Fourier-Transform infrared spectroscopy (FT-IR)

Introduction

Bioplastics[1] have lately gained increasing attention because their biosynthesis can alleviate the production problem of oil-based synthetic plastics resulting from possible shortage of oil. In contrast to synthetic plastics, bioplastics have the fundamental advantage of being biodegradable. The great advantage of bioplastics – the conservation of fossile resources and reduction of CO_2 emissions – make them one of the most important innovations for sustainable development.

In the present research the degradation processes of poly(ε-caprolactone) (PCL)[2] and poly(L-lactic acid) (PLA)[3,4] were studied. PCL is a semi-crystalline, linear, aliphatic polyester which can be produced from ε-caprolactone. It is a commercial biodegradable polymer with good mechanical properties and is frequently used as blend component.[2] PLA can be produced by polycondensation of lactic acid or by ring-opening polymerization of the cyclic lactide dimer. The monomeric raw material can be obtained from renewable agricultural sources such as corn. PLA is already used for several applications such as plastic bottles or coated papers for food and beverage packaging.

Polyhydroxyalkanoates (PHA)[5–7] are nature's high molecular weight thermoplastic polyesters which are occurring in the storage granules of a variety of bacteria. In the present study the most common member of the PHAs, poly(3-hydroxybutyrate) (PHB), was blended with PCL and PLA. PHB has the disadvantage of being stiff and brittle, but the mechanical properties can be significantly enhanced by blending PHB with PCL and PLA.

The combination of thermogravimetric analysis (TGA) and FT-IR spectroscopy[8–10] is a powerful technique for the study of polymer decomposition. Based on such measurements, it is possible to achieve

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a quantitative and qualitative characterization of the decomposition products.

The results of the thermogravimetric analysis of PHB[11–14], PCL[13,15] and PLA[13,16,17] in nitrogen atmosphere were reported in several publications. PHB decomposes mainly to crotonic acid and at higher temperatures to carbon dioxide and propene. 5-hexenoic acid and ε-caprolactone are the main degradation products of PCL. PLA decomposes to acetaldehyde, carbon dioxide and carbon monoxide and at higher temperature to a dilactide. We have studied the decomposition of PHB in oxygen atmosphere[14] and detected the additional evolution of carbon monoxide. Thus, also the thermal degradation of PLA and PCL in oxygen atmosphere will be of interest because in future applications biodegradable polymers will be decomposed by waste combustion in air.

To identify the overlapped absorption bands in the FT-IR gas-phase spectra of the decomposition products 2D-correlation analysis was used in some cases. Generalized 2D correlation spectroscopy, first proposed by Noda,[18,19] is a versatile tool for the analysis of a set of spectroscopic data collected for a system under some type of external perturbation.

Experimental Part

Materials

Bacterially synthesized poly(3-hydroxybutyrate) (Sigma-Aldrich, $M_w = 437{,}000$ g/mol), poly(L-lactic acid) containing 10% meso-lactic acid (NatureWorks LLC, Minnesota, USA) and poly(ε-caprolactone) (Sigma-Aldrich, $M_w = 65{,}000$ g/mol, $M_n = 42{,}500$ g/mol) were used without further purification for the TGA/FT-IR experiments. For the preparation of blends the polymers were dissolved in chloroform p.A. and films were cast by evaporation of the chloroform at 35 °C.

Instrumentation

TGA experiments were carried out on a Netzsch STA 409 PC *Luxx*® system coupled by a heated transfer line (volume 50 mL; heated at 180 °C) to a Bruker Tensor™ IR spectrometer with a liquid-cooled mercury cadmium telluride (MCT) detector. Samples of 28–42 mg were heated with a heating rate of 10 °C/min. from 40 to 720 °C. The flow rate of the carrier gas (nitrogen or oxygen) was 50 mL/min. FT-IR gas-phase spectra were collected with a spectral resolution of 4 cm^{-1} and 32 scans were coadded per spectrum. The TG response and the Gram-Schmidt curves, which represent the amount of decomposition products at a particular temperature, were recorded simultaneously to the FT-IR spectra.

2D Correlation Spectroscopy

The 2D correlation spectra were calculated with the *2Dshige* software (http://sci-tech.ksc.kwansei.ac.jp/~ozaki/main-eng.htm). 2D Correlation spectroscopy has a characteristic pair of synchronous $\Phi(\nu_1, \nu_2)$ and asynchronous $\Psi(\nu_1, \nu_2)$ 2D correlation spectra in which the two spectral variables ν_1 and ν_2 are wavenumbers. In the case of TGA/FT-IR measurements the spectral data sets are collected under the external perturbation of increasing temperature. The mathematical fundamentals of 2D correlation analysis are described in detail elsewhere.[18,19]

Results and Discussion

Degradation of Poly(ε-caprolactone)

Figure 1 A shows the TGA and Gram-Schmidt curves of PCL measured on-line to the thermal decomposition in nitrogen atmosphere. The TGA curve displays a one-step degradation. There is a slight initial increase of the TGA trace detectable, which is determined by thermal buoyancy of the sample holder. This small artefact is also observable in the other degradation experiments. The weight loss observed in the TGA trace is accompanied by a simultaneous increase in the Gram-Schmidt curve at about 360 °C. After a

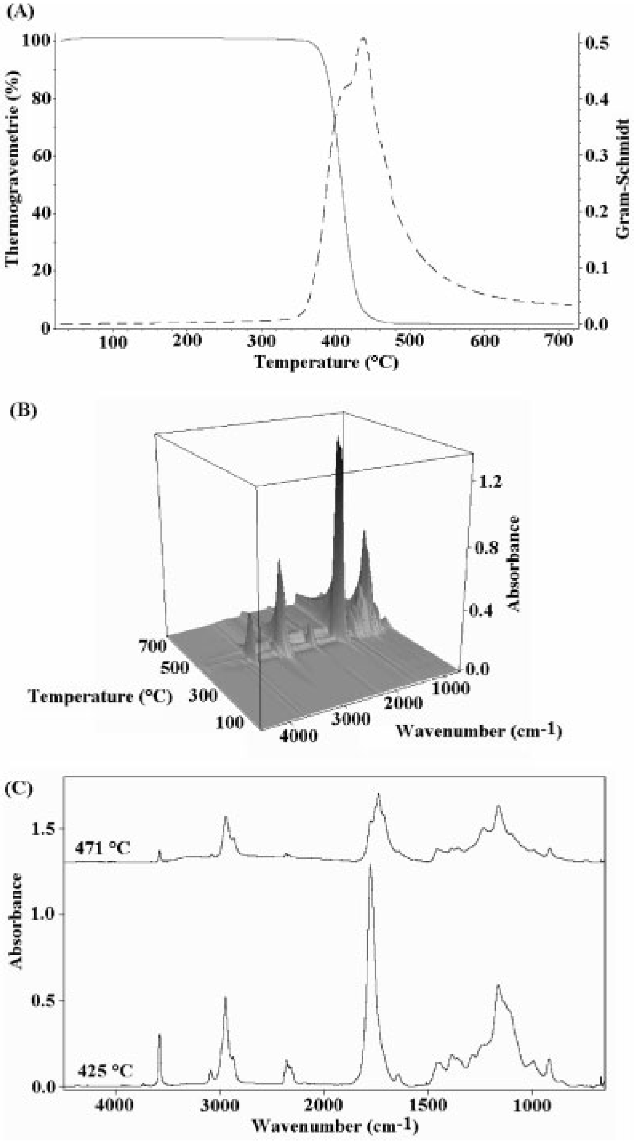

Figure 1.

TGA (—) and Gram-Schmidt (---) curves of the thermal degradation of PCL in nitrogen (A), temperature-dependent 3D FT-IR spectra (B) and characteristic spectra recorded at different temperatures (C).

shoulder at 400 °C the Gram-Schmidt curve reaches a peak maximum at about 450 °C and then decreases until the end of the experiment at 720 °C.

Figure 1 A agrees with the 3D FT-IR spectra of the degradation process shown in Figure 1 B. Similar to the TGA curve, beyond 340 °C the first decomposition products are detectable. Figure 1 C shows the FT-IR spectra recorded at 425 °C and 471 °C. The spectrum recorded at 425 °C can be assigned to the main decomposition product 5-hexenioc acid and its di- and trimers with bands at 3575 cm^{-1} ν(OH), 3087 cm^{-1} ν(H-C=C), 2945 cm^{-1} $\nu_{as}(CH_2)$, 2877 cm^{-1} $\nu_{s}(CH_2)$, 1778 cm^{-1} ν(C=O),

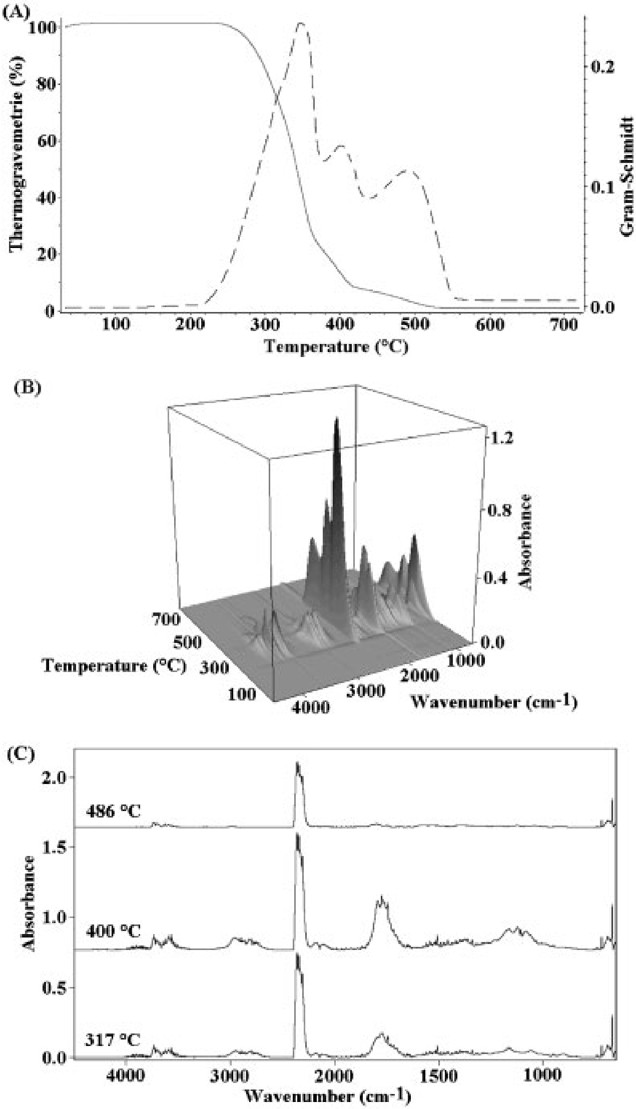

Figure 2.
TGA (—) and Gram-Schmidt (---) curves of the thermal degradation of PCL in oxygen (A), temperature-dependent 3D FT-IR spectra (B) and characteristic spectra recorded at different temperatures (C).

1642 cm^{-1} ν(C=C), 1432 cm^{-1} δ(CH$_2$), 1164 and 1107 cm^{-1} ν(C–O) and 950 and 915 cm^{-1} γ(R–C=CH$_2$). Additionally, carbon dioxide (2349 cm^{-1}) and traces of carbon monoxide (2176/2117 cm^{-1}) could be detected. Furthermore, at temperatures >430 °C ε-caprolactone is evolved (Figure 1C, 471 °C), which can be identified by its characteristic band at 1736 cm^{-1} ν(C=O). With a further rise in temperature the evolution of 5-hexenoic acid and ε-caprolactone are decreasing and increasing, respectively.

Figure 3 presents the synchronous (A) and asynchronous (B) 2D correlation spectra (2400-1600 cm^{-1}) of the thermal degradation of PCL in nitrogen atmosphere in the temperature range 143–430 °C. In the synchronous spectrum only the ν(C=O)

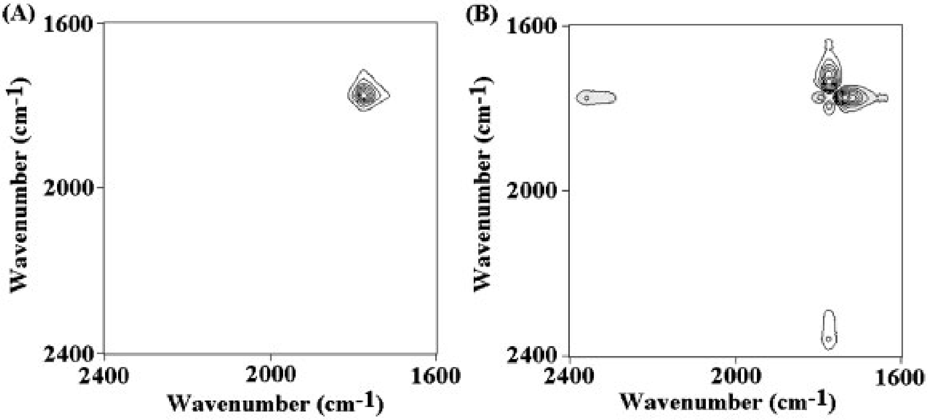

Figure 3.

Synchronous (A) and asynchronous (B) 2D correlation spectra (2400–1600 cm^{-1}) calculated from the temperature-dependent FT-IR spectra of the PCL decomposition in nitrogen atmosphere for the temperature range 143–430 °C (negative cross peaks are grey-shaded).

auto peak of 5-hexenioc acid at 1778 cm^{-1} is displayed. In contrast, several cross peaks are visible in the asynchronous spectrum. The positive cross peak (1778, 2350) indicates that 5-hexenoic acid develops before carbon dioxide. Furthermore, the negative cross peak (1736, 1778) indicates that 5-hexenoic acid is evolved before ε-caprolactone. Figure 2 A shows the TGA and Gram-Schmidt curves of the thermal decomposition of PCL in oxygen atmosphere. In contrast to the one-step decomposition in nitrogen the TGA curve decreases in three steps (220 °C, 360 °C and 420 °C). The corresponding Gram-Schmidt curve also shows three peaks in the range of the three steps of the TGA-curve. In the 3D FT-IR spectra (Figure 2 B) decomposition products are first observable beyond 220 °C. The spectra measured within the temperature range of the three steps of the TGA-curve are displayed in Figure 2 C. The spectrum at 317 °C reflects strong band intensities for carbon dioxide (ν(O=C=O) 2349 cm^{-1}, δ(O=C=O) 667 cm^{-1} and the combination vibration at 3724 cm^{-1}) Additionally, carbon monoxide (2176/2117 cm^{-1}) and water (ν(H-O) at 3900–3400 cm^{-1} and δ(H-O) at 1800–1300 cm^{-1}) could be identified. The rest of the bands belongs to short-chain acids and their di- and trimers: 3589 cm^{-1} ν(O–H), 2952 cm^{-1} $\nu(CH_2)$, 2816 cm^{-1} ν(CH), 1778 cm^{-1} ν(C=O), 1164 and 1107 cm^{-1} ν(C–O). 2D correlation spectroscopy did not provide additional information about these absorption bands.

Degradation of Poly(L-lactic acid)

The thermal decomposition of PLA was also analyzed in nitrogen and oxygen atmosphere. Figure 4 A shows the TGA and Gram-Schmidt curves obtained in nitrogen atmosphere. The degradation takes place in one step beyond 300 °C. In the Gram-Schmidt trace also only one peak is observable, but decomposition products are detectable at higher temperatures. The 3D FT-IR spectra are displayed in Figure 4 B and decomposition products are also detectable beyond 300 °C. Initially mainly acetaldehyde (3475 cm^{-1} ($2 \times \nu$(C=O)), 2968 cm^{-1} ($\nu(CH_3)$), 2740 cm^{-1} (ν(CHO)), 1762 cm^{-1} (ν(C= O)), 1414 + 1371 cm^{-1} ($\delta(CH_3)$), 1127 cm^{-1} (ν(C–O)), carbon dioxide (2349 cm^{-1}) and carbon monoxide (2174/2116 cm^{-1}) develop (Figure 4 C, 352 °C). At higher temperature (Figure 4 C, 425 °C) also lactide (3,6-dimethyl-1,4-dioxan-2,5-dione) is detectable by bands at 3008 cm^{-1} (ν(CH)), 2952 cm^{-1} ($\nu_{as}(CH_3)$), 2893 cm^{-1} ($\nu_s(CH_3)$), 1795 cm^{-1} (ν(C=O)),

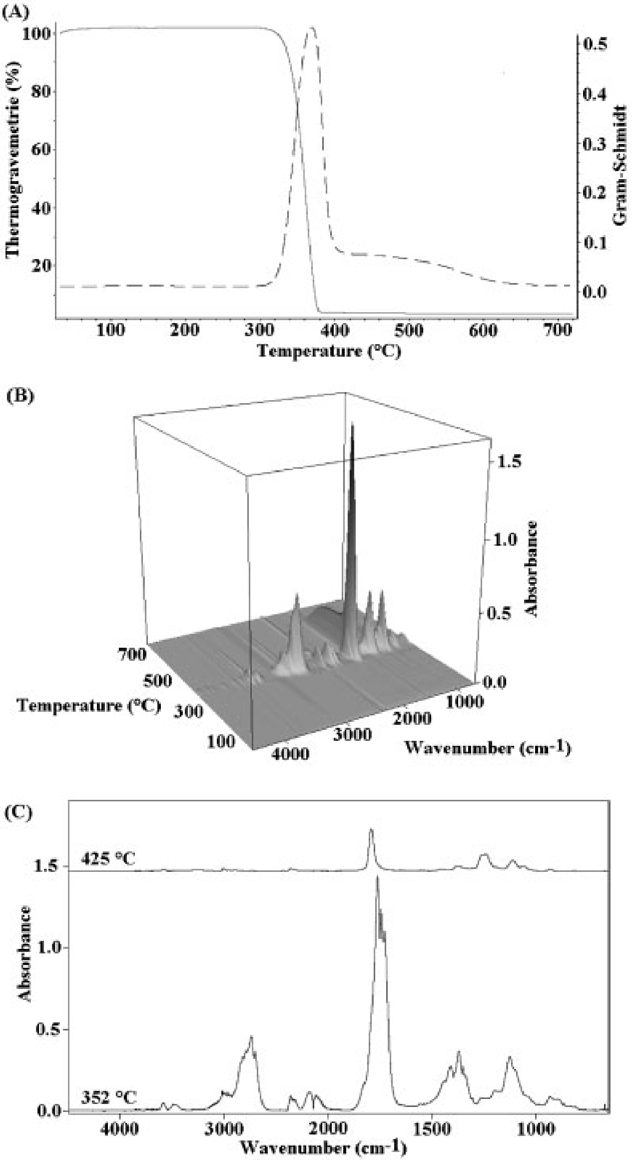

Figure 4.
TGA (—) and Gram-Schmidt (---) curves of the thermal degradation of PLA in nitrogen (A), temperature-dependent 3D FT-IR spectra (B) and characteristic spectra recorded at different temperatures (C).

1365 cm^{-1} ($\delta(CH_3)$), 1248 cm^{-1} and 1108 cm^{-1} (ν(C–O–C)) and 935 cm^{-1}.[20] Water (3900–3400 cm^{-1} and 1800–1300 cm^{-1}) and methane (3200–2900 cm^{-1} and 1400–1200 cm^{-1}) are detectable only in traces. In order to extract more information 2D correlation spectroscopy was applied to these spectral data. In Figure 6 A and B the synchronous and asynchronous spectra in the 2400–1600 cm^{-1} region are shown for the temperature range 143–430 °C. In the synchronous spectrum only an auto peak of the ν(C=O) absorption is shown. The asynchronous spectrum provides more

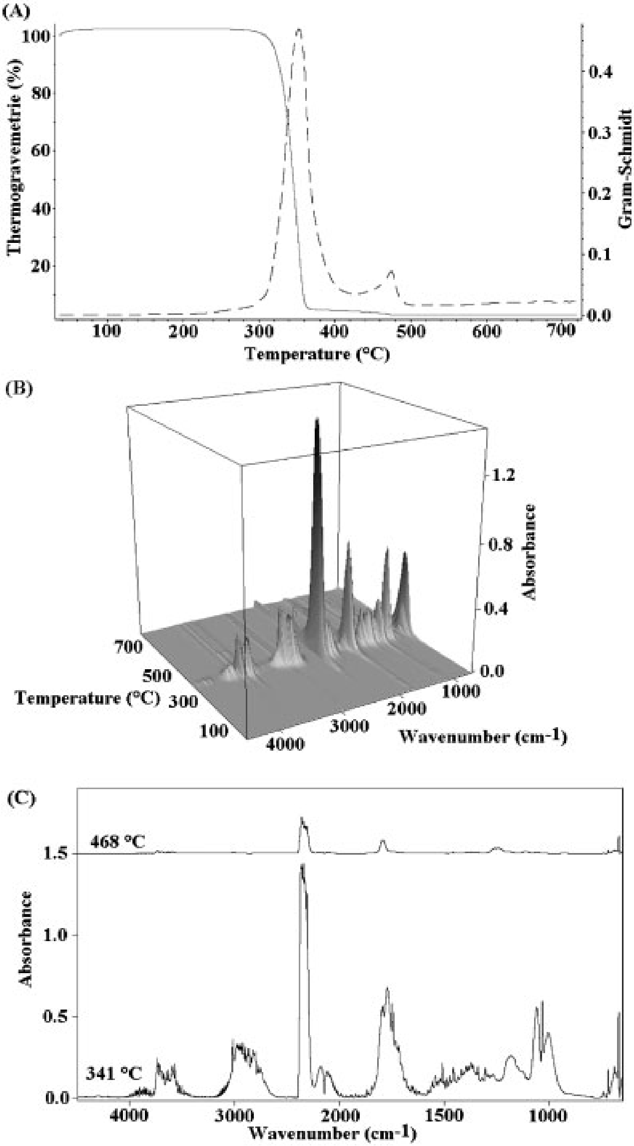

Figure 5.

TGA (—) and Gram-Schmidt (---) curves of the thermal degradation of PLA in oxygen (A), temperature-dependent 3D FT-IR spectra (B) and characteristic spectra recorded at different temperatures (C).

detailed information. The negative cross peak (1795, 2350 cm^{-1}) and the positive cross peak (1743, 2350 cm^{-1}) indicate that carbon dioxide develops before lactide but after acetaldehyde. Also carbon monoxide is evolved before lactide as indicated by the negative cross peaks at (1795, 2185) and (1795, 2111). Cross peaks are also observable for different $\nu(C{=}O)$ absorption bands. The negative cross peak (1795, 1743) belongs to lactide (1795 cm^{-1}) and acetaldehyde (1743 cm^{-1}) and allows the conclusion that lactide develops after acetaldehyde. Furthermore, a negative cross peak at (1795, 1831) is detected. The band at 1831 cm^{-1} develops simultaneously with a band at 1778 cm^{-1} and this doublet can be tentatively assigned to acetic anhydride.[21]

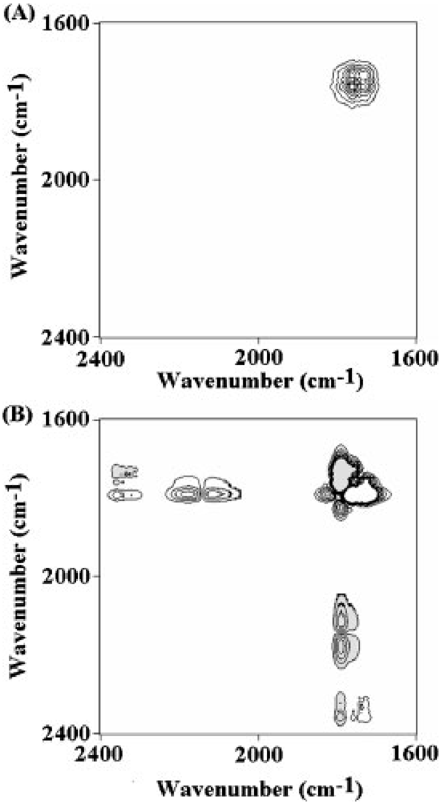

Figure 6.
Synchronous (A) and asynchronous (B) 2D correlation spectra (2400–1600 cm^{-1}) calculated from temperature-dependent FT-IR spectra of the PLA decomposition in nitrogen atmosphere for the temperature region 143–430 °C (negative cross peaks are grey-shaded).

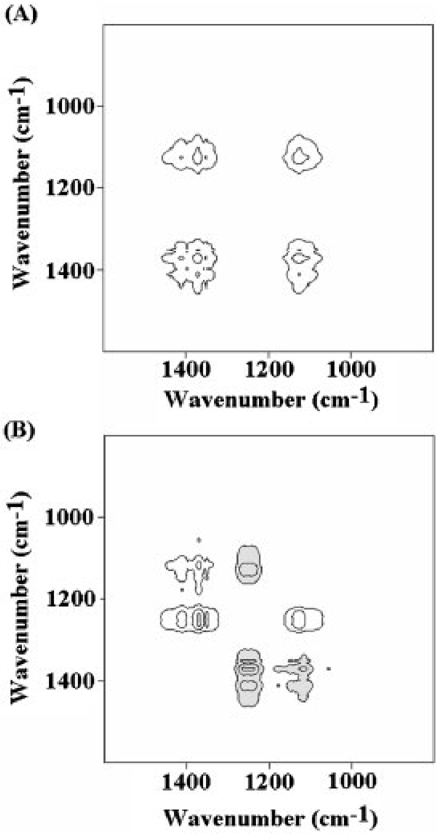

Figure 7.
Synchronous (A) and asynchronous (B) 2D correlation spectra (1600–800 cm^{-1}) calculated from temperature-dependent FT-IR spectra of the PLA decomposition in nitrogen atmosphere for the temperature region 143–430 °C (negative cross peaks are grey-shaded).

Thus, lactide is obviously evolved after acetic anhydride. Acetic acid[22] is also detectable as illustrated by the ν(O–H) band at 3586 cm^{-1}. The ν(C=O) band of acetic acid, however, is overlapped by the band of acetic anhydride at 1778 cm^{-1}. In Figure 7 A and B the synchronous and asynchronous spectra between 1600–800 cm^{-1} are displayed for the temperature range 143–430 °C. The synchronous spectrum shows two auto peaks and corresponding positive cross peaks at 1376 cm^{-1} and 1126 cm^{-1}. Both bands belong to acetaldehyde and therefore develop simultaneously. The asynchronous spectrum shows a positive cross peak at (1126, 1251) and negative cross peaks at (1108, 1376) and (1251, 1376). This also proves that acetaldehyde develops before lactide.

Furthermore, the degradation process of PLA in oxygen atmosphere was analyzed. The TGA and Gram-Schmidt curves of the decomposition of PLA in oxygen atmosphere are shown in Figure 5 A. The TGA curve shows a large and a small weight-loss step at 300 °C and 470 °C, respectively. The Gram-Schmidt curve has a large peak maximum at 355 °C and a much smaller one at 475 °C. Figure 5 B displays the corresponding 3D FT-IR spectra. For a better identification of the characteristic decomposition products at different temperatures the spectra recorded at 341 °C and 468 °C are mapped in Figure 5 C. Similar to the degradation of PCL in oxygen PLA also oxidizes in the first step to carbon dioxide, carbon monoxide, water and short-chain acids (absorption band assignments are described in detail in the section on PCL) and their di- and trimers. The small TGA step at 470 °C is characteristic of the evolution of carbon dioxide and lactide. Thus, also in oxygen atmosphere lactide develops in the decomposition of PLA at higher temperatures.

Degradation of Poly(3-hydroxybutyrate) Blends

Figure 8 A shows the TGA and Gram-Schmidt curves of a PHB/PCL (50:50 wt%) blend in nitrogen atmosphere. The weight

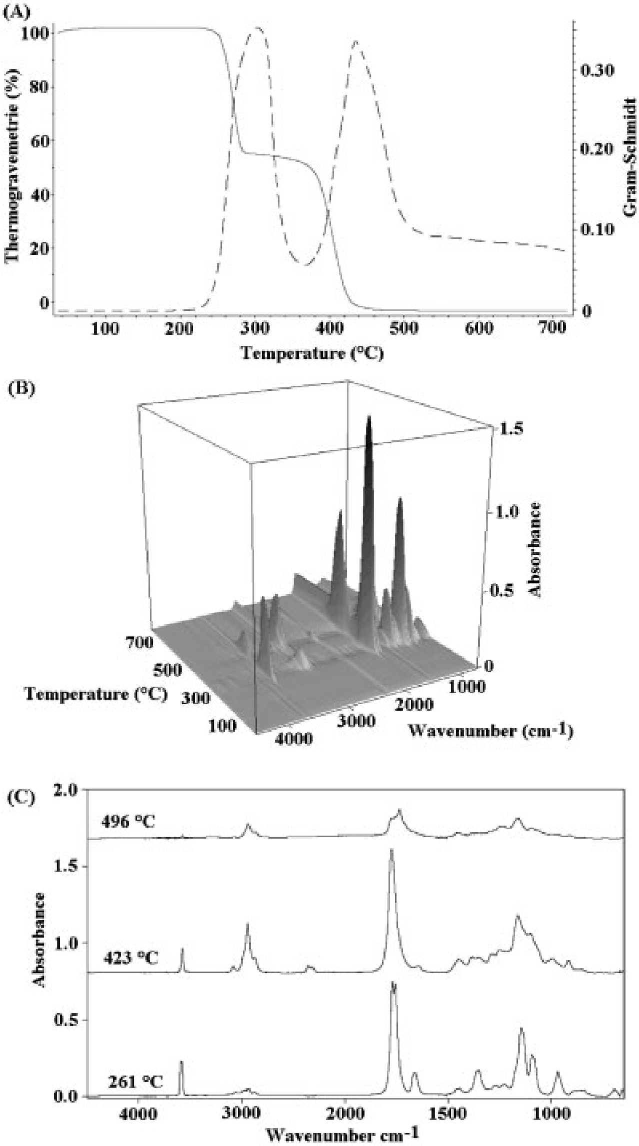

Figure 8.

TGA (—) and Gram-Schmidt (---) curves of the thermal degradation of a PHB/PCL (50:50 wt%) blend in nitrogen (A), temperature-dependent 3D FT-IR spectra (B) and characteristic spectra recorded at different temperatures (C).

loss occurs in two sharp steps with onset temperatures at 260 °C and 380 °C. Accordingly, the Gram-Schmidt curve presents two peaks between 230–370 °C and 370–520 °C. Beyond 520 °C the Gram-Schmidt trace continues at an elevated level. Thus, even at 720 °C decomposition products are detectable.

Figure 8 B displays the corresponding 3D FT-IR spectra of the PHB/PCL (50:50 wt%) blend decomposition in nitrogen. Two temperature regions with high spectral intensities can be distinguished around 300 °C and 450 °C. Individual spectra of these temperature ranges are illustrated in Figure 8 C. The spectrum at 261 °C shows

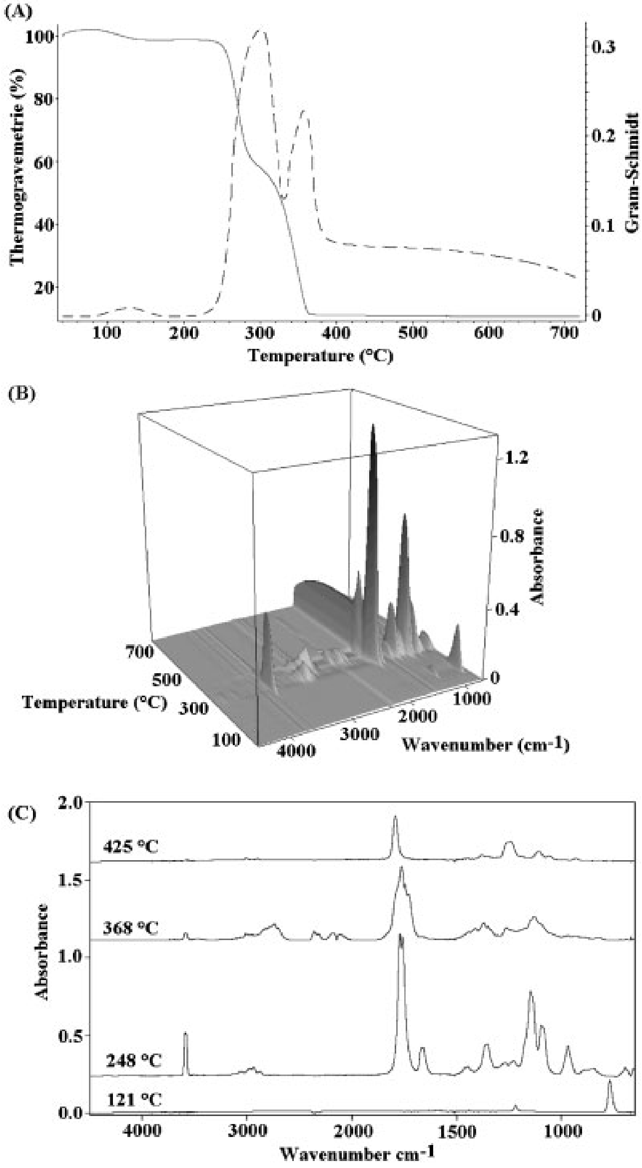

Figure 9.

TGA (—) and Gram-Schmidt (---) curves of the thermal degradation of a PHB/PLA (50:50 wt%) blend in nitrogen (A), temperature-dependent 3D FT-IR spectra (B) and characteristic spectra rcorded at different temperatures (C).

the main decomposition product of PHB, crotonic acid, which can be identified by its typical absorption bands: ν(O–H) 3589 cm^{-1}, ν(C–H) from 3074 to 2865 cm^{-1}, ν(C=O) 1760 cm^{-1}, ν(C=C) 1660 cm^{-1}, δ(C–H) 1450 cm^{-1}, δ(CH_3) 1357 cm^{-1}, ν(C–O) 1145 + 1097 cm^{-1} and γ(trans-C=C) 967 cm^{-1}. The absorption at 691 cm^{-1} (γ(cis-C=C)) is characteristic for the cis-configuration of crotonic acid. At 423 °C 5-hexenoic acid, the main decomposition product of PCL, can be identified by the absorption bands discussed in the previous section on PCL. Additionally, carbon dioxide (2349 cm^{-1}) and traces of carbon monoxide (2176/2117 cm^{-1}) are detectable. Furthermore, at temperatures > 430 °C ε-caprolactone is evolved (Figure 8 C, 496 °C) and can be identified by its characteristic ν(C=O) absorption at 1736 cm^{-1}. Thus, the PHB/PCL (50:50 wt%) blend decomposes in a step-wise mechanism similar to the individual blend components.

Figure 9 A shows the TGA and Gram-Schmidt curves of a PHB/PLA (50:50 wt%) blend in nitrogen atmosphere. Again, the TGA curve has two sharp weight-loss steps at 260 °C and 330 °C. For both steps corresponding peaks are detectable in the Gram-Schmidt trace. A small weight loss is also detectable at about 100 °C. In Figure 9 B the 3D FT-IR spectra for this decomposition process are mapped.

Two temperature ranges of high absorption intensities around 310 °C and 370 °C can be identified preceded by a region of low-intensity spectra at about 100 °C. Individual spectra of these regions are shown in Figure 9 C. The spectrum at 121 °C with only two bands at 1220 cm^{-1} and 771 cm^{-1} could be identified as chloroform which was not completely removed from the blend during sample preparation. The spectrum at 248 °C reflects the major decomposition product of PHB, crotonic acid. At 386 °C acetaldehyde, carbon dioxide and carbon monoxide - the decomposition products of PLA - are detectable. Finally, at 425 °C the PLA-specific product lactide could be detected. Thus, in analogy to the PHB/PCL blend, the PHB/PLA blend also decomposes in two steps which correspond to the individual blend components.

Conclusion

PCL and PLA undergo completely different degradation processes in nitrogen and oxygen atmosphere. This is in contrast to PHB where the main decomposition product is crotonic acid in both environments and otherwise only small differences could be found for the degradation in nitrogen and oxygen.[14]

As already reported,[13,15] PCL decomposes in nitrogen atmosphere at 340 °C to 5-hexenioc acid and carbon dioxide and at temperatures >430 °C ε-caprolactone is evolved. Additionally, traces of carbon monoxide could be identified. 2D correlation spectroscopy established that 5-hexenoic acid develops before carbon dioxide.

PLA decomposes in nitrogen atmosphere to acetaldehyde, carbon dioxide, carbon monoxide, water and methane. With increasing temperature lactide becomes the major degradation product. This is in agreement with the results reported in other publications.[16,17] By 2D correlation spectroscopy it was found that acetaldehyde develops before carbon dioxide and lactide.

In oxygen atmosphere, on the other hand, PCL and PLA decompose into carbon dioxide, carbon monoxide, water and short-chain acids. At higher temperatures the formation of lactide was observed for PLA.

The polymer blends PHB/PCL (50:50 wt%) and PHB/PLA (50:50 wt%) decompose in nitrogen atmosphere in two-step mechanisms which resemble the individual blend components. In both blends PHB was decomposed first mainly to crotonic acid and after this process PCL and PLA degraded at higher temperatures to their established decomposition products. No shift in the onset temperatures of the decomposition of the individual homopolymers was detectable due to blend formation.

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