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Crystallization Behavior of Poly(3-hydroxybutyrate) (PHB), Poly(ε-caprolactone) (PCL) and Their Blend (50:50 wt.%) Studied by 2D FT-IR Correlation Spectroscopy

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Summary: Variable-temperature FT-IR spectra of poly(3-hydroxybutyrate) (PHB), poly(ε-caprolactone) (PCL) and a PHB/PCL (50:50 wt.%) blend were analyzed by two-dimensional correlation spectroscopy (2DCOS). For this purpose the ν(C=O) region was employed to characterize in some detail the crystallization behavior of the investigated polymer systems during cooling from the melt. The asynchronous 2D correlation spectra clearly captured the existence of three components in the crystallinity-sensitive region of the C=O stretching mode for PHB and PCL, respectively: a well-ordered, an inter-mediate and a less ordered crystalline state. Furthermore, by 2DCOS application a sequential order of the observed structural changes could be proposed for the whole temperature range during the crystallization of both polymers. In the case of the PHB/PCL (50:50 wt.%) polymer blend, we have split up the spectral data set in the sub-sets between 200–120 °C and 70–30 °C for a more detailed 2DCOS analysis. In this way we could separate the crystallization process of PHB and PCL in the polymer blend.

Keywords: crystallization; FT-IR Spectroscopy; generalized 2D correlation spectroscopy (2DCOS); Poly(3-hydroxybutyrate) (PHB); Poly(ε-caprolactone) (PCL)

Introduction

The crystallization process of polymers that transfers the entangled melt into a semicrystalline state is one of the most important research topics in polymer physics and has been investigated in several publications.[1–5] However, the understanding of the crystallization process of polymers based on the knowledge of the molecular mobility controlling the transformation is still insufficient. In general, the formation of an ordered structure during the crystallization of polymer domains depends on the crystallization conditions.[6] The present study describes the mechanism of the crystallization of poly(3-hydroxybutyrate) (PHB), poly(ε-caprolactone) (PCL) and a PHB/PCL blend with a composition of 50:50 wt.% by gradual cooling from the melt. The investigated polymers are semicrystalline bioplastics and they have the great advantage over conventional plastics of being biodegradable.[7]

Polyhydroxyalkanoates (PHA)[8–10] are intracellular polyesters which are synthesized by bacteria. The linear and stereo regular optically active polyesters are composed of 3-hydroxyfattyacid monomers. The best known and most used PHA representative is poly(3-hydroxybutyrate) (PHB). However, for many applications the high melting point, close to the thermal degradation temperature and the considerable brittleness of PHB are unfavorable properties.[11,12] Therefore, it has been the aim to overcome these weaknesses by preparing blends of PHB.

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Poly(ε-caprolactone) (PCL)[13–15] is a commercial bioplastic and it has the great advantage over other synthetic polymers of being biodegradable. Thus, it can be degraded by enzymes from several microorganisms. PCL is a semi-crystalline linear polymer with good mechanical properties. It has a melting point of about 60 °C and has a great potential as biomaterial.

In previous investigations variable-temperature FT-IR spectroscopy has been applied to PHB homopolymer and PHB copolymers with hydroxyvalerate (P(HB-co-HV) or hydroxyhexanoate P(HB-co-HHx).[16–20] From these measurements a first insight into the crystallinity and conformational changes in heating/cooling cycles was obtained and allowed the assignment of state-of-order specific absorption bands in the investigated spectra. However, the superposition of spectral features sometimes limits the utility of FT-IR spectroscopy. In such cases generalized two-dimensional correlation spectroscopy (2DCOS)[21–23] is a useful technique to provide a better understanding of the investigated phenomena even in the case of complicated spectral intensity variations of strongly superimposed absorption bands. It has been shown, however, that the interpretation of new absorption bands derived from the 2D correlation spectra as well as the derivation of sequential orders has to be performed with care because artefacts may be introduced by the subtraction routine underlying the dynamic spectra series.[31,32] Some research groups have characterized PHB and its copolymers by 2D correlation spectroscopy and observed the coexistence of two crystallinity sensitive bands in the ν(C=O) region.[24–27] In previous studies,[28,29] we have also analyzed the impact of annealing PHB, the melting of PCL and PHB/PCL polymer blends on the ν(C=O) region by variable-temperature FT-IR spectroscopic investigations in combination with 2DCOS. In case of non-annealed PHB a recrystallization process was detected between 30–120 °C. Furthermore, the asynchronous 2D correlation spectrum resolved two ν(C = O) bands each for the crystalline (highly ordered at 1718 cm^{-1} and less ordered at 1724 cm^{-1}) and amorphous (slightly ordered and disordered at 1737 and 1747 cm^{-1}, respectively) regions. During the melting in the temperature range 120–200 °C similar results were detected for non-annealed and annealed PHB. Therefore, the existence of two crystalline ν(C=O) bands was established and only one absorption band was identified for the amorphous (1747 cm^{-1}) region. For the melting behavior of PCL between 30 and 70 °C only two ν(C=O) bands (crystalline (1724 cm^{-1}), amorphous (1737 cm^{-1})) were identified. In case of the PHB/PCL blend perturbation correlation moving window 2D (PCMW2D) correlation analysis allowed the separation of the heating behavior into three processes (melting of PCL, recrystallization of PHB and melting of PHB).

The present communication focuses on variable-temperature FT-IR spectroscopic measurements to obtain information on the changes in the ν(C=O) spectral region, which is splitted into crystalline and amorphous absorption bands during the crystallization of PHB and PCL homopolymers and a PHB/PCL (50:50 wt.%) blend. However, the analysis of these spectral variations is not straightforward, because the absorption bands are heavily overlapped. Therefore, the aim of the present study is to apply 2DCOS to separate the overlapping bands arising from crystalline and amorphous parts of PHB and PCL. Furthermore, in the case of the PHB homopolymer and the PHB/PCL blend, the spectral data sets are split up in different temperature ranges to investigate the two blend components by 2DCOS in more detail.

Experimental Part

Materials

Bacterially synthesized poly(3-hydroxybutyrate) (PHB) (Sigma-Aldrich, Mw = 437,000 g/mol) and poly(ε-caprolactone)

(PCL) (Sigma-Aldrich, $M_n = 80{,}000$ g/mol) were used for the experiments. For the sample preparation, the polymer was dissolved in hot chloroform and a film was cast on a KBr pellet by evaporation of the chloroform at 35 °C for 1 hour.

Instrumentation

The FT-IR spectra of the film samples were measured with a Bruker IFS 28 FT-IR spectrometer equipped with a mercury cadmium telluride (MCT) detector. The FT-IR spectra were collected with a spectral resolution of 4 cm^{-1} and 32 scans were coadded per spectrum. The temperature of the sample cell that holds the KBr-pellets with PHB, PCL and the blend of PHB/PCL (50:50 wt.%) blend films was varied by using a temperature controller unit of Hotset RR 210. The PCL film was cooled with a decrement of 5 °C over a temperature range of 70–30 °C, the PHB and the PHB/PCL blend films were cooled with a decrement of 10 °C over the temperature interval of 200–30 °C. After changing the temperature, the cell was maintained at that temperature for 10 minutes to equilibrate the sample.

Generalized 2D Correlation Spectroscopy

Generalized 2D correlation spectroscopy was first proposed by Noda in 1993 and the mathematical fundamentals are described in detail elsewhere.[20–23] 2DCOS creates a pair of synchronous $\Phi(\nu_1, \nu_2)$ and asynchronous $\Psi(\nu_1, \nu_2)$ 2D correlation spectra where the spectral variables ν_1 and ν_2 are wavenumbers. The synchronous 2D correlation intensity represents the overall similarity or coincidental changes between two separate spectral variables during variation of an external perturbation (in the present case decreasing of the temperature). The asynchronous 2D correlation spectrum monitors variations in spectral intensities that are not synchronously correlated. The 2D correlation spectra were calculated by the software "2Dshige" (Kwansei Gakuin University, Japan). For this purpose the experimental FT-IR data sets were extracted and only the region of the ν(C=O) absorption band (1780–1690 cm^{-1}) was used for analysis. In the 2D correlation spectra, white-colored regions are defined as positive correlation intensities, while gray-colored regions represent negative correlation intensities.

Results and Discussion

Crystallization Behavior of Poly(3-hydroxybutyrate) (PHB)

Figure 1 (bottom) shows the FT-IR spectra of PHB in the 1780–1690 cm^{-1} region measured at 200 and 30 °C. In the top of Figure 1 the second derivatives of the spectra recorded at 200 and 30 °C are represented. These data reveal that there are at least two bands in the ν(C=O) band region. One is located at 1740 cm^{-1}. This absorption band is intense at 200 °C, but its intensity decreases during the temperature decrease and becomes only a shoulder at the lowest temperature of 30 °C.[16–19] Thus, this band is characteristic of the amorphous regions of PHB. The other band near 1724 cm^{-1} completely disappears in the spectrum measured at 200 °C but becomes

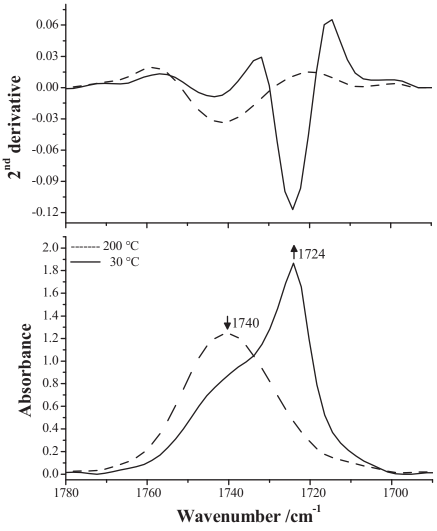

Figure 1.
FT-IR spectra of the ν(C=O) band region of PHB at 200 and 30 °C (top: second derivatives; bottom: original spectra).

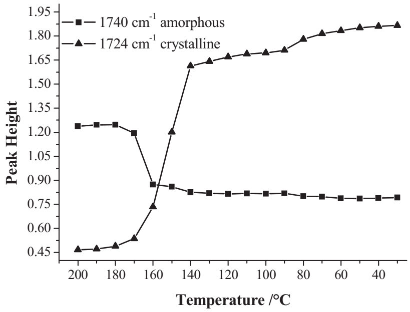

Figure 2.
The peak intensities of the ν(C=O) bands of the amorphous (1740 cm^{-1}) and the crystalline (1724 cm^{-1}) regions of PHB as a function of temperature.

the dominant absorption at 30 °C. This band is therefore assigned to the ν(C=O) band of the crystalline regions.[16–19]

Figure 2 shows the peak height versus temperature plot for the amorphous (1740 cm^{-1}) and the crystalline (1724 cm^{-1}) absorption bands. The intensity of the amorphous absorption band (1740 cm^{-1}) decreases below 180 °C and simultaneously, a significant increase of the 1724 cm^{-1} band can be observed. In the temperature range 140–30 °C a slight further intensity decrease can be detected for the 1740 cm^{-1} band. The band at 1724 cm^{-1} shows the opposite behavior: it slightly increases and achieves the highest intensity at 30 °C.

For a more detailed 2DCOS analysis the experimental temperature range was split up into the sub-ranges 200–120 °C and 120–30 °C. First the temperature range 200–120 °C where the main spectral changes can be observed will be discussed. Figure 3 shows the synchronous (A) and asynchronous (B) 2D correlation spectra based on the spectral changes in the wavenumber range 1780–1690 cm^{-1}. In the synchronous spectrum (Figure 3A) two autopeaks are developed at (1745, 1745) and (1724, 1724) cm^{-1} together with a pair of negative cross peaks at (1745, 1724) cm^{-1}, indicating the opposite spectral variations of the amorphous an d crystalline domains during the crystallization of PHB. In the corresponding asynchronous 2D spectrum (Figure 3B), three pairs of cross peaks appear at (1745, 1724), (1727, 1724) and (1724, 1718) cm^{-1}. It should be noted that the asynchronous 2DCOS spectrum resolves three overlapped bands for the crystalline regions and one for the amorphous state (1745 cm^{-1}) of the ν(C=O) vibrational mode. We have assigned the crystalline bands to less ordered (1727 cm^{-1}), intermediately ordered (1724 cm^{-1}) and perfectly ordered (1718 cm^{-1}) crystalline domains. In a previous study, Zhang et al.[30] investigated the spectral changes and molecular dynamics of PHB during the isothermal crystallization process at 129 °C. By using conventional spectral analysis

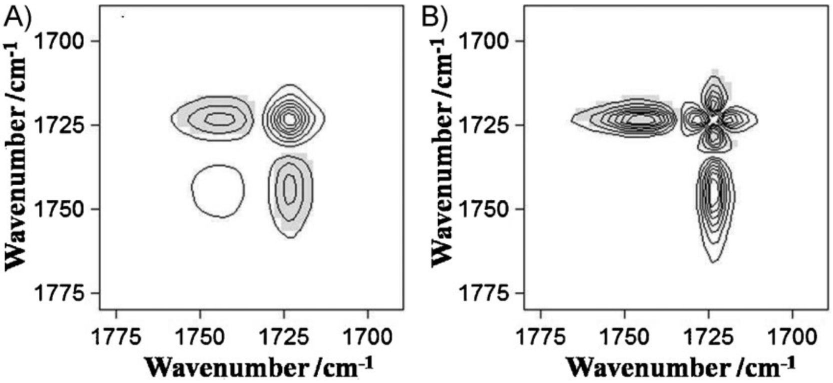

Figure 3.
Synchronous (A) and asynchronous (B) 2D correlation spectra of the ν(C=O) region for the crystallization process (200–120 °C) of PHB.

methods together with 2DCOS, they observed two amorphous ν(C=O) absorption bands at 1747 and 1739 cm^{-1}. However, it should be mentioned that the cooling process was completely different from the one described in this work. The presence of asynchronous cross peaks indicates the out-of-phase intensity changes of the correlated bands. Because $\Phi(1745, 1724) < 0$ the asynchronous cross peak $\Psi(1745, 1724) < 0$ changes sign and becomes positive.[21–23] This indicates, that during the crystallization process the decrease in intensity of the amorphous ν(C=O) band at 1745 cm^{-1} and the intensity increase of the crystalline band at 1724 cm^{-1} do not occur simultaneously. Therefore, the amorphous regions (1745 cm^{-1}) change before the less ordered crystalline domains (1724 cm^{-1}) are formed. The second cross peak at (1727, 1724) cm^{-1} has a positive sign and reflects a correlation between the less ordered and intermediate crystalline regions. This correlation indicates that the formation of the crystalline regions with the lowest perfection (1727 cm^{-1}) takes place before the intermediate (1724 cm^{-1}) crystalline domains are formed. Furthermore, the asynchronous 2D correlation spectrum developed a negative cross peak for the two crystalline regions (1724, 1718) cm^{-1}. This observation indicates that the formation of the highly ordered crystalline domains and that of the less ordered crystalline regions takes place out of phase. Thus, the formation of the perfectly ordered crystalline regions (1718 cm^{-1}) proceeds prior to the less ordered crystalline structures during the crystallization of PHB.

From the asynchronous 2D correlation spectrum (Figure 3B), it can be concluded that with decreasing temperature the absorption intensities change as follows (the symbol "<" means change prior to):

$$(1745, 1727, 1718 < 1724)\,\mathrm{cm}^{-1}$$

This result suggests that the amorphous regions (1745 cm^{-1}) disappear, while the lowest ordered (1727 cm^{-1}) and the highest ordered crystalline domains (1718 cm^{-1}) are formed. Towards lower temperature the lowest ordered (1727 cm^{-1}) crystallites are transformed into intermediate (1724 cm^{-1}) crystalline regions.

Additionally, the 2DCOS analysis has also been applied for the 120–30 °C temperature variation. Figure 4 displays the corresponding synchronous (A) and asynchronous (B) 2D correlation spectra. Based on the synchronous 2D correlation spectrum (Figure 4A) only one autopeak at (1724, 1724) cm^{-1} is detected, due to the main spectral variations. The asynchronous 2DCOS spectrum displayed in Figure 4B resolves two pairs of cross peaks at (1743, 1726) and (1726, 1720) cm^{-1}. The first cross peak has a negative sign, which represents a correlation between the amorphous (1743 cm^{-1}) and less ordered (1726 cm^{-1}) crystalline domains. Additionally, the positive cross peak at (1726, 1720) cm^{-1} reveals that the spectral variations of the less ordered (1726 cm^{-1}) and perfectly ordered (1720 cm^{-1}) crystalline absorption bands take place out of phase.

Based on the asynchronous 2D correlation spectrum (Figure 4B) the following sequential order of intensity changes can be proposed for the 120–30 °C temperature range:

$$(1726 < 1720, 1743)\,\mathrm{cm}^{-1}$$

This sequence indicates that during further cooling the less ordered (1726 cm^{-1}) crystalline regions are transformed into crystallites with highest perfection (1720 cm^{-1}), followed by the disappearance of the residual amorphous (1743 cm^{-1}) domains.

Crystallization Behavior of Poly(ε-caprolactone) (PCL)

Figure 5 displays the FT-IR spectra of the ν(C=O) region (bottom) of PCL and their second derivatives (top) measured at 70 and 30 °C. Similarly to the cooling process of PHB two major absorption bands are observed in the wavenumber region 1780–1690 cm^{-1}. The band at 1736 cm^{-1}, which is

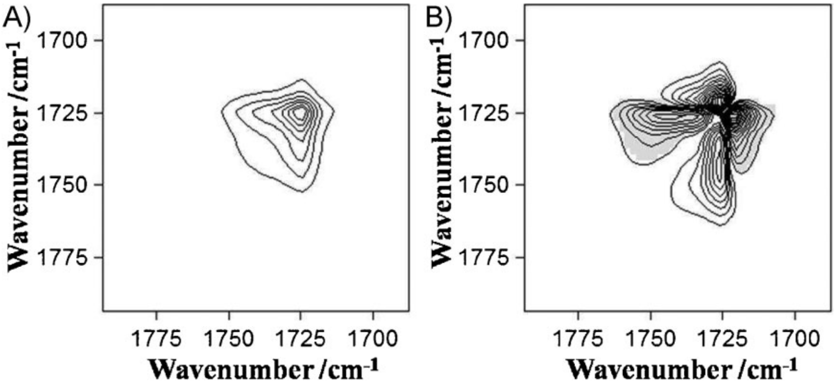

Figure 4.
Synchronous (A) and asynchronous (B) 2D correlation spectra of the ν(C=O) region for the crystallization process (120–30 °C) of PHB.

characteristic of the amorphous regions dominates at 70 °C and disappears almost completely at 30 °C. The band at 1724 cm^{-1} is a crystallinity-sensitive band, which has its highest intensity at 30 °C and disappears at 70 °C.

From the peak height intensity plot of the amorphous (1736 cm^{-1}) and crystalline (1724 cm^{-1}) ν(C=O) absorption bands versus temperature (Figure 6), it can be concluded that the crystallization process takes place at 55 °C. This result is confirmed by the significant intensity decrease of the 1736 cm^{-1} band beyond 55 °C, whereas the crystallinity band shows the opposite behavior.

For a more detailed analysis of the structural changes during the crystallization process of PCL 2DCOS was applied to the spectral data recorded between 70–30 °C. Figure 7 shows the synchronous (A) and the asynchronous (B) 2D correlation spectra of the wavenumber region 1780–1690 cm^{-1}.

In the synchronous 2D correlation spectrum of the ν(C=O) region two autopeaks occur at (1737, 1737) and (1722, 1722) cm^{-1} together with two negative cross peaks at (1737, 1722) cm^{-1} indicating the opposite spectral variations of the crystalline and amorphous regions

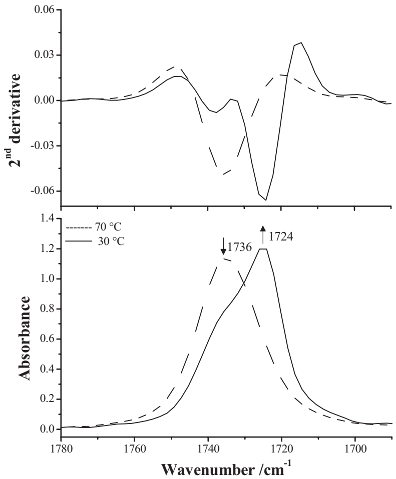

Figure 5.
FT-IR spectra of the ν(C=O) spectral region of PCL measured at 70 and 30 °C (top: second derivatives; bottom: original spectra).

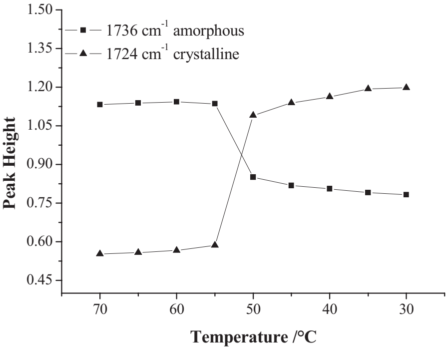

Figure 6.
The peak intensity variations of the 1736 (amorphous) and 1724 cm^{-1} (crystalline) ν(C=O) absorption bands of PCL versus temperature.

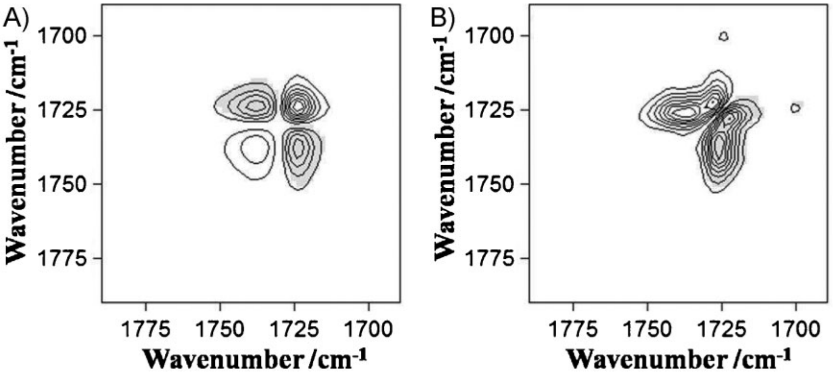

Figure 7.
Synchronous (A) and asynchronous (B) 2D correlation spectra of the ν(C=O) band of PCL in the temperature range 70–30 °C.

during the cooling process of PCL. In the corresponding asynchronous 2D correlation spectrum (Figure 7B) two pairs of cross peaks are located at (1737, 1726) and (1728, 1722) cm^{-1}. Similarly to the PHB homopolymer during the crystallization process the ν(C=O) absorption band of PCL can be resolved into three crystallinity-sensitive bands (1728, 1726 and 1724 cm^{-1}) arising from different states of order. Furthermore, only one amorphous band can be detected at 1736 cm^{-1} during the crystallization process of PCL. The positive cross peak at (1736, 1726) cm^{-1} reflects a correlation between the amorphous regions and the intermediate crystalline domains of PCL. It indicates that amorphous regions disappear before less ordered crystalline domains are formed. Finally, the positive cross peak at (1728, 1722) cm^{-1} reflects a correlation of two overlapped crystalline absorption bands and allows to deduce that crystalline regions with the lowest perfection (1728 cm^{-1}) are formed before the crystallites with highest perfection (1722 cm^{-1}).

It should be pointed out, that in our previous study of the melting behavior of PCL only one crystalline absorption band at 1726 cm^{-1} was detected.[29] Especially, the observation of the absorption band at lowest wavenumber position indicates an almost perfect crystalline state as a consequence of the organization of the PCL chains during the slow cooling.

Crystallization Behavior of a PHB/PCL (50:50 wt.%) Polymer Blend

Figure 8 shows the FT-IR spectra and their second derivatives in the ν(C=O) region of the PHB/PCL (50:50 wt.%) polymer blend film at 200, 120 and 30 °C. The band complex consists of two major contributions: a sharp band at 1724 cm^{-1} and a broad feature near 1740 cm^{-1}. The band at 1740 cm^{-1} has the highest intensity at

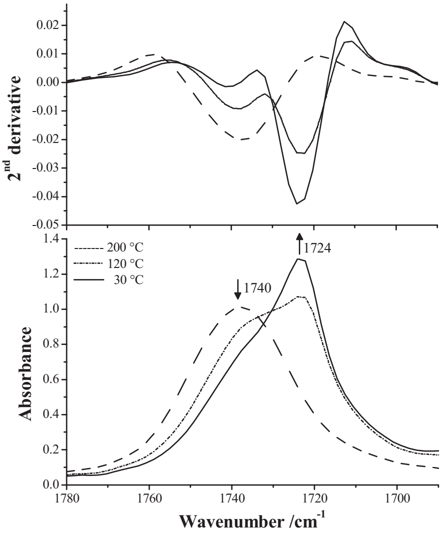

Figure 8.
Temperature-dependent FT-IR spectral variations in the ν(C=O) region of the PHB/PCL (50:50 wt.%) blend film. The spectra measured at 200, 120 and 30 °C (top: second derivatives; bottom: original spectra).

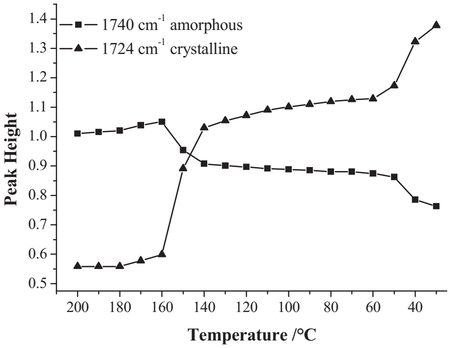

Figure 9.
Peak maximum intensity of the ν(C=O) bands, which are characteristic of the amorphous (1740 cm^{-1}) and the crystalline (1724 cm^{-1}) domains of the PHB/PCL polymer blend as a function of temperature.

200 °C. At lower temperatures its intensity decreases and is only observable as a broad shoulder at 30 °C. The band at 1724 cm^{-1} demonstrates the opposite behavior during the cooling process of the PHB/PCL (50:50 wt.%) blend film: it disappears at 200 °C and is most intense at 30 °C. Thus, the bands at 1740 cm^{-1} and 1724 cm^{-1} are obviously characteristic of the amorphous and crystalline regions, respectively.

Figure 9 displays a plot of the peak height versus temperature for the amorphous (1740 cm^{-1}) and crystalline (1724 cm^{-1}) absorption bands. At high temperatures the intensity at 1724 cm^{-1} is almost constant until 160 °C and then increases significantly between 160 °C and 130 °C. This is a consequence of the crystallization process of PHB. In the temperature range between 130–70 °C this band further increases slightly. Finally, between 60–30 °C a sharp increase is observed which can be assigned to the crystallization of PCL. In comparison, the intensity of the amorphous band at 1740 cm^{-1} shows an opposite behavior at the different temperature regions described above.

In what follows the crystallization process of the PHB and PCL blend components will be discussed in more detail by a 2DCOS analysis. Figure 10 and 11 depict the synchronous (A) and asynchronous (B) 2D correlation spectra based on the spectral changes in the wavenumber region 1780–1690 cm^{-1} for the temperature ranges 200–120 °C (Figure 10) and 70–30 °C (Figure 11). The temperature range 200–120 °C primarily reflects the crystallization behavior of PHB. The synchronous 2D correlation spectrum (Figure 10A) shows spectral changes of two major bands at 1747 and 1724 cm^{-1}, which are confirmed by the presence of two auto peaks. The pair of negative cross peaks at (1747, 1724) cm^{-1} indicates the opposite spectral variations of the amorphous (1747 cm^{-1}) and the crystalline (1724 cm^{-1}) absorption bands. In the asynchronous 2D correlation spectrum (Fig. 10B) two cross peaks are located at (1743, 1724) and (1724, 1718) cm^{-1}. The

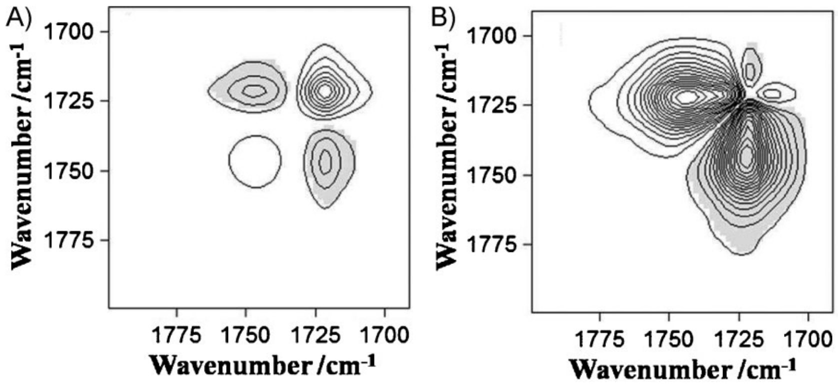

Figure 10.
Synchronous (A) and asynchronous (B) 2D correlation spectra of the ν(C=O) band region of the PHB/PCL (50:50 wt.%) blend in the temperature range 200–120 °C.

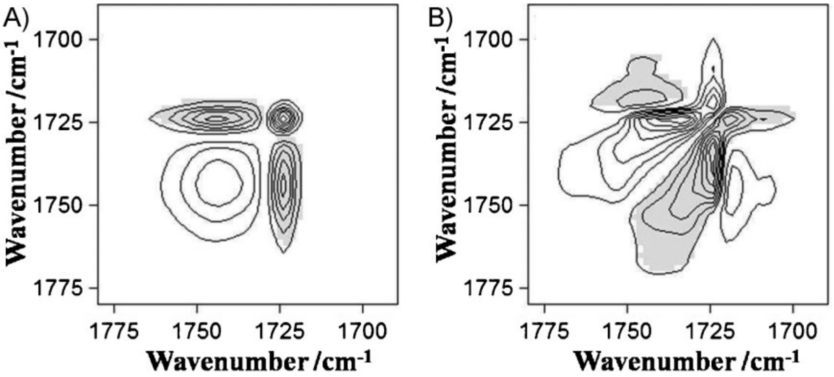

Figure 11.
Synchronous (A) and asynchronous (B) 2D correlation spectra of the ν(C=O) spectral region in the temperature range 70–30 °C of the PHB/PCL (50:50 wt.%) blend.

positive cross peak (1743, 1724) cm^{-1} proves that the amorphous regions disappear prior to the formation of crystalline domains with some disorder (intermediate state). The cross peak at (1724, 1718) cm^{-1} has a negative sign and is characteristic for the structural changes of two crystalline regions of PHB. The well-ordered crystalline state (1718 cm^{-1}) appears before the intermediate crystalline state (1724 cm^{-1}).

In summary the following sequential order is established for the temperature range 200–120 °C from the asynchronous 2D correlation spectrum (Figure 10B):

$$(1743,\ 1718 < 1724)\ \mathrm{cm}^{-1}$$

Based on the 2DCOS analysis the disappearance of the amorphous regions (1743 cm^{-1}) and the formation of the perfectly ordered crystalline (1718 cm^{-1}) domains take place at the same time. In the last step the intermediate crystalline (1724 cm^{-1}) regions are formed during the crystallization of PHB in the PHB/PCL blend.

In the temperature range 70–30 °C primarily the crystallization process of PCL is monitored. In the synchronous 2D correlation spectrum (Figure 11A) two auto peaks are developed at 1745 and 1724 cm^{-1} together with a pair of negative cross peaks at (1745, 1724) cm^{-1}. These are characteristic of the opposite intensity variations of the amorphous and crystalline regions during the temperature decrease. In the corresponding asynchronous 2D correlation spectrum (Figure 11B) three cross peaks are identified at (1745, 1718), (1736, 1724) and (1724, 1718) cm^{-1}. Thus, the asynchronous spectrum resolves two absorption bands for the crystalline regions at 1724 cm^{-1} (intermediately ordered) and 1718 cm^{-1} (perfectly ordered). Additionally, during the crystallization of PCL two bands for the amorphous regions can be observed, which are assigned to completely amorphous (1745 cm^{-1}) and amorphous domains with some order (1736 cm^{-1}). The first cross peak has a negative sign and reflects a correlation between the completely amorphous state (1745 cm^{-1}) and the highest ordered crystalline regions (1718 cm^{-1}). Thus, during the crystallization process of PCL, crystallites with the highest perfection are formed before the completely amorphous regions disappear. From the positive cross peak at (1736, 1724) cm^{-1} it can be derived that the amorphous regions with some order (1736 cm^{-1}) disappear before intermediately ordered crystalline regions (1724 cm^{-1}) are formed. Accordingly, the positive cross peak at (1724, 1718) cm^{-1} reflects a correlation between the intermediately ordered crystalline state and the perfectly ordered crystalline state of PCL. Thus, the intermediately ordered (1724 cm^{-1}) crystalline domains are formed before the perfectly ordered (1718 cm^{-1}) regions.

Based on the asynchronous 2D correlation spectrum shown in Figure 11B the following sequential order for the temperature range 70–30 °C of the PHB/PCL (50:50 wt.%) blend can be derived:

$$(1736 < 1724 < 1718 < 1745)\,\mathrm{cm}^{-1}$$

This result establishes that the amorphous regions with some structural order (1736 cm^{-1}) crystallize before intermediately ordered crystalline domains (1724 cm^{-1}) are transformed into perfectly ordered crystalline regions (1718 cm^{-1}). In the last step, the less ordered amorphous regions disappear (1745 cm^{-1}) during the crystallization process of PCL in the PHB/PCL polymer blend.

Conclusion

In the present study the structural changes of PHB, PCL and a PHB/PCL (50:50 wt.%) polymer blend were studied by variable-temperature FT-IR spectroscopy in combination with a 2DCOS analysis.

Based on the 2DCOS analysis a complete sequential order of the structural changes could be proposed for the crystallization process of PHB and PCL in the homopolymers and the blend during cooling from the melt. Both polymers showed the coexistence of three crystalline ν(C=O) absorption bands, which were assigned to different states of order: perfectly ordered crystalline regions, intermediately ordered crystalline domains and less ordered crystalline regions. In summary, the 2DCOS study for the ν(C=O) band complex suggested that the disappearance of the amorphous regions takes place while crystallites with some disorder are formed. In other words, the initial crystal growth occurs by the formation of less ordered crystallites. Once these crystallites are formed, the further growth of highly ordered crystals, which are characterized by the absorption band at the lowest wavenumber position, will occur. During further cooling less ordered crystallites reorganize into intermediately ordered crystals.

For the PHB/PCL (50:50 wt.%) blend the crystallization processes of PHB and PCL were studied separately. Thus, in the temperature range between 200–120 °C the crystallization process of PHB takes place. Contrary to the cooling process of the PHB homopolymer during the crystallization of PHB in the polymer blend only two crystalline absorption bands were detected and assigned to intermediately (1724 cm^{-1}) and perfectly ordered (1718 cm^{-1}) crystalline domains. Therefore, in the temperature range 200–120 °C the amorphous regions of PHB disappear and perfectly ordered crystalline domains are formed before the intermediately ordered crystalline domains are detected. For the temperature range between 70–30 °C the crystallization of PCL takes place and the existence of two crystalline (1724 and 1718 cm^{-1}) and two amorphous (1736 and 1745 cm^{-1}) ν(C=O) bands were identified by 2DCOS analysis. At first the amorphous regions with some structural order (1736 cm^{-1}) crystallize before the intermediately ordered crystalline regions (1724 cm^{-1}) are transformed into the perfectly ordered crystallites (1718 cm^{-1}). At last, the completely amorphous regions (1745 cm^{-1}) disappear in final cooling process.

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