Details of thermal behavior of spin-coated film of biodegradable poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) copolymer studied by principal component analysis-based two-dimensional (PCA2D) correlation spectroscopy

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Abstract
Principal component analysis-based two-dimensional (PCA2D) correlation spectroscopy was applied to the temperature-dependent infrared-reflection absorption (IRRAS) spectra of a spin-coated film of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (P(HB-co-HHx) (HHx = 7.2 mol%) copolymer. In asynchronous PCA2D correlation spectra, we clearly captured the existence of two components in the crystalline band of the C=O stretching mode, well-ordered primary crystals observed at lower wavenumber and less ordered secondary crystals observed at higher wavenumber, which is not readily detectable in the original 1D spectra. Furthermore, the intensity changes of bands at 1298 and 1280 cm⁻¹ are significantly different in the temperature ranges below and above the transition temperature around 140 °C identified by the 2D first derivatives plot. The result further confirms that the sequence of intensity changes with increasing temperature is such that bands for less ordered crystalline components of P(HB-co-HHx) (HHx = 7.2 mol%) are changing first at an earlier (i.e., lower temperature) stage.

1. Introduction

Polymer thin films have recently received much attention due to their potential applications in various fields of polymer science and nanotechnology [1–3]. For the successful applications of polymer thin films used in a wide range of temperature, it is very important to understand the thermal properties of polymer thin films. The molecular structure and orientation of polymer in the thin films must be investigated because they strongly affect the physical properties, such as their thermal transition behavior. Poly( hydroxyalkanoate) (PHA) polymers, which are biodegradable and renewable polymers, are one of the most innovative materials for packing and have promising application as tissue engineering. Among PHA polymers, poly(3-hydroxybutyrate) (PHB) and PHB-based copolymers, such as poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (P(HB-co-HHx)), have been studied extensively as environment-friendly polymers [4–7]. The structure and thermal behavior of PHB and P(HB-co-HHx) copolymers have been investigated by X-ray diffraction, differential scanning calorimetry, FTIR spectroscopy, and two-dimensional (2D) correlation spectroscopy [8–15].

Generalized 2D correlation spectroscopy is a well-established analytical technique that provides considerable utility and benefit in various studies of polymers [15–18]. Some of the notable features of generalized 2D correlation spectra are: enhancement of spectral resolution by spreading peaks along the second dimension; establishment of unambiguous assignments through the correlation of bands of selectively coupled by various interaction mechanisms; and determination of the sequence of the spectral peak emergence.

To improve the data quality for 2D correlation analysis, we recently proposed a powerful development in generalized 2D correlation spectroscopy which involves the incorporation of multivariate chemometrics techniques [19–25]. Principal component analysis-based 2D (PCA2D) correlation showed the great advantage, especially in the noise suppression for generalized 2D correlation spectroscopy [19,23]. The details of this technique were described previously [19–25].

We have also proposed a new 2D data presentation scheme to determine the transition temperature of polymers [26,27]. A set of...
spectra $A(\nu, T)$, where $\nu$ is the wavenumber and $T$ is the temperature, is differentiated with respect to $T$ to create the set of first derivatives of form $dA/dT$. The 2D mapping representation that plots the values of the first derivatives of the absorbance with respect to temperature over the space of temperature versus wavenumber on a single map provides a surprisingly simple and direct method for detecting the transition temperatures. The location of the minima or maxima in this 2D mapping enables us to determine the transition temperature of polymers.

In this study, the details of thermal behavior of the spin-coated film of biodegradable P(HB-co-HHx) (HHx = 7.2 mol%) copolymer is investigated using PCA2D correlation spectroscopy. Its transition temperature is determined by the 2D mapping representation that plots the values of the first derivatives of the absorbance with respect to temperature over the space of temperature versus wavenumber on a single map.

2. Experimental

Biodegradable P(HB-co-HHx) (HHx = 7.2 mol%) copolymer was obtained from the Procter & Gamble Company, Cincinnati, OH, USA. It was dissolved in hot chloroform, and then precipitated in hexane. The same process repeated again and re-precipitated in methanol, and vacuum-dried at 60 °C. Pt-coated silicon wafers from Siltron Inc. (Korea) were used as the substrates for spin coating. To prepare the spin-coated films, about 0.5 wt% P(HB-co-HHx) (HHx = 7.2 mol%) solution dissolved in chloroform was spun onto a Pt-coated silicon wafer at 3500 rpm for 60 s. The thickness of P(HB-co-HHx) (HHx = 7.2 mol%) spin-coated film was 60 nm.

The infrared-reflection absorption (IRRAS) spectra were measured at a spectral resolution of 4 cm$^{-1}$ with a Bruker (Karlsruhe, Germany) IFS 66v/s FT-IR spectrometer equipped with a liquid nitrogen-cooled MCT detector. A Bruker A513 reflection attachment, which includes a heating block attachment, was used for the IRRAS measurement, and a p-polarized infrared ray was used at an angle of incidence of 82°. The p-polarized infrared ray was generated by a SPECAC (Orpington, UK) wire-grid infrared polarizer. To ensure a high signal-to-noise ratio, 1024 interferograms were co-added for each measurement. Both sample and source compartments were evacuated to 1 mbar.

Prior to a PCA calculation, the mean centering operation was applied to the data matrix. To preserve the amplitude information of the variation of spectral intensities, which becomes important later for a 2D correlation analysis, other steps commonly used in PCA, such as normalization scaling of data according to the standard deviation, were not carried out. PCA analysis was performed in Pirouette software (Infometrix Inc.). Synchronous and asynchronous 2D correlation spectra were obtained using the same software as at described previously [19–25].

3. Results and discussion

The temperature-dependent IRRAS spectra of spin-coated film of P(HB-co-HHx) (HHx = 7.2 mol%) copolymer, obtained during the heating process from 30 to 150 °C, are shown in Fig. 1. There are two distinct bands in the C=O stretching band, a crystalline band at 1725 cm$^{-1}$ and an amorphous band near 1747 cm$^{-1}$. Fig. 2 gives the 2D map of $dA/dT$ as a function of wavenumber and temperature. The highest value of $dA/dT$ is observed near 140 °C for all bands. Thus, the transition temperature of spin-coated film of P(HB-co-HHx) (HHx = 7.2 mol%) copolymer determined by 2D map is about 140 °C, which is relatively close to the melt temperature of corresponding bulk P(HB-co-HHx) (HHx = 7.2 mol%) copolymer sample [6,7].

Fig. 1. IRRAS spectra of spin-coated film of P(HB-co-HHx) (HHx = 7.2 mol%) during heating from 30 to 150 °C at an interval of 5 °C.

We applied PCA2D correlation spectroscopy to the temperature-dependent IRRAS spectra of P(HB-co-HHx) (HHx = 7.2 mol%). The original spectral data set (Fig. 1) was decomposed into scores and loading vectors by standard PCA analysis. PC1, PC2, and PC3 accounts for 95.01%, 4.83%, and 0.11%, respectively, of the contribution to the data; thus, three principal components have essentially all information needed to describe the transition-temperature-dependent IRRAS spectra of P(HB-co-HHx) (HHx = 7.2 mol%). We formulated the reconstructed data matrix $A^*(A^* = WV^T)$, which no longer contains the residual (i.e., noise) contributions, from a few selected significant scores and loadings derived from PCA of the original set of perturbation-dependent spectra A. Here, $W$ and $V$ are a score matrix and a loading matrix, respectively. The notation $V^T$ stands for the transpose of $V$. The reconstructed data matrix, $A^*$, obtained by the product of score and loading vector of from the three principal components, was used instead of the original raw spectral data matrix, $A$, for a subsequent 2D correlation analysis.

Fig. 3(a) and (b) show the synchronous and asynchronous 2D correlation spectrum constructed from the PCA-reconstructed data with three PCs. Power spectrum extracted along the diagonal line on the synchronous 2D correlation spectrum is also shown at the top of Fig. 3(a). Inserted is the enlarged spectrum

Fig. 2. 2D map of $dA(\nu, T)/dT$ as function of $\nu$ and $T$. Here, $\nu$ is the wavenumber and $T$ is the temperature.
for $\text{C=O}$ stretching bands. The band at 1296 cm$^{-1}$ assigned to C–O–C stretching band in synchronous 2D correlation spectrum (Fig. 3(a)) is clearly resolved into two bands at 1300 and 1281 cm$^{-1}$ in the asynchronous 2D correlation spectrum (Fig. 3(b)). In the synchronous 2D correlation spectra in the $\text{C=O}$ stretching bands (inserted spectrum in Fig. 3(a)), we can mainly observe the crystalline band at 1725 cm$^{-1}$ and the amorphous band at 1747 cm$^{-1}$. However, the band at 1725 cm$^{-1}$ now seems to be resolved into two bands at 1722 and 1731 cm$^{-1}$ in the asynchronous 2D correlation spectrum (inserted spectrum in Fig. 3(b)), which is not readily detectable in the original 1D spectra. The crystalline band may look like an ordinary single peak in the original IRRAS spectra, but it turned out to be a doublet from the 2D correlation analysis. We clearly captured the possible existence of two components in the crystalline band of the $\text{C=O}$ stretching mode, i.e., well-ordered primary crystals observed at a lower wavenumber and less ordered secondary crystals observed at a higher wavenumber [25].

Fig. 4(a) and (b) show the slice spectra at 1722 and 1747 cm$^{-1}$ in the synchronous PCA2D correlation spectrum (Fig. 3(a)). Fig. 4 clearly shows that 1381, 1295, 1230, 1103, and 1058 cm$^{-1}$ are assigned to the crystalline components P(HB-co-HHx) (HHx = 7.2 mol%), while 1254, 1194, 1120, and 1083 cm$^{-1}$ are assigned to the amorphous components.

Fig. 5(a) and (b), show synchronous PCA2D correlation spectra constructed from the spectral data obtained in the temperature ranges below and above the transition temperature of 140 °C, respectively. Very interestingly, the intensity change of the band at 1298 cm$^{-1}$ is much more significant at temperatures lower than the transition temperature (Fig. 5(a)), while that at 1280 cm$^{-1}$ becomes more significant at higher temperatures (Fig. 5(b)). On the basis of results given in Fig. 5, we can conclude that bands at 1298 and 1280 cm$^{-1}$ are assigned to less ordered and well-ordered crystalline
components, respectively. It is in a good agreement with the analysis of 2D correlation spectra shown in Fig. 3 that the sequence of intensity changes with increasing temperature is such that a band at 1731 cm\(^{-1}\) assigned to less ordered crystalline component is changing first at an earlier (i.e., lower temperature) stage.

4. Conclusion

In this study, the thermal behavior of the spin-coated film of biodegradable P(HB-co-HHx) (HHx = 7.2 mol%) copolymer was successfully investigated for the first time by using PCA2D correlation spectroscopy. From the PCA2D correlation spectra, we conclude that the sequence of intensity changes with increasing temperature is such that bands for less ordered crystalline component are changing first at an earlier (i.e., lower temperature) stage. The transition temperature of spin-coated film of P(HB-co-HHx) (HHx = 7.2 mol%) determined by 2D mapping representation that plots the values of the first derivatives of the absorbance with respect to temperature over the space of temperature versus wavenumber on a single map is 140 °C. Thus, we can clearly identify details of thermal behavior of spin-coated film of P(HB-co-HHx) (HHx = 7.2 mol%) by using PCA2D correlation analysis.

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References