Study on the higher-order structure and hydrogen bonding of biodegradable polymer by low-frequency vibrational spectroscopy

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Abstract. Biodegradable polymer is preferred material to replace the conventional petroleum based polymer materials to protect the nature and conserve oil supplies. Information related to higher-order structure and hydrogen bonding among polymers can be observed in the low-frequency region (3.3–333 cm⁻¹) using terahertz (THz) spectroscopy. THz spectra measurement of temperature-dependent investigation of poly(3-hydroxybutyrate) (PHB) homopolymer and polymer blend of PHB/glycol chitosan with the blend ratios of (80/20) and (60/40) have been performed to investigate the change in higher-order structure and intermolecular hydrogen bonding formed by polymer blends of PHB and glycol chitosan. The THz spectra revealed that the peak at 82 cm⁻¹ does not collapse even in the high temperature indicating the important role of hydrogen bonding interaction between poly(3-hydroxybutyrate) (PHB) and glycol chitosan in maintaining the higher-order structure of the PHB in its blending system.

1. Introduction

Polymer have been an important part of our daily life to be easier and better. They can be found almost in all sorts applications from the car we drive to the television we watch, from the food we eat to the refrigerators they are store in, from the contact lens we use to the medicine we take. However, most of them, are made of conventional fuel-based polymers such as polyethylene (PE) and polypropylene (PP) which are not biodegradable. They cannot be decomposed in natural environment causing many environmental problems and harmful for living organisms. Therefore, biodegradable polymer is preferred as a promising material to replace petroleum-based polymer used in contact with living organisms [1,2]. It is characterized by biocompatibility, biodegradability, non-toxicity, and adsorptive ability which is suitable for cosmetics, pharmaceutical, food industries, and biomedical engineering applications [3]. Among the biodegradable polymers, chitosan is abundant in nature. It is a polysaccharide produced by deacetylation of chitin and is extensively used in drug delivery applications [4,5]. However, chitosan is difficult to use industrially because it has high glass transition temperature (Tg) and high crystallinity. Therefore, it is necessary to improve their physical properties by blending or copolymerizing with other polymers. In this study, we modified glycol chitosan, a water soluble chitosan derivate with a highly demand poly(3-hydroxybutyrate) (PHB). The PHB/glycol chitosan polymer blend will enhance its degradability [6].

The number of conventional methods, X-ray diffraction, infrared (IR) spectroscopy, UV-Vis
spectroscopy, mass spectroscopy (MS), and nuclear magnetic resonance spectroscopy (NMR) has been well introduced to understand the structures and properties of biodegradable polymers. [6-8]. However, there is newly developing spectroscopic method in low-frequency vibrational region which still under explored [9,10]. The region of low-frequency vibrational spectroscopy or widely known as terahertz (THz) lies between wavenumber range from 3.3–333 cm$^{-1}$. Vibrational bands of molecules in this region arise from both inter and intramolecular interaction of the molecules. Therefore, the spectra are sensitive to the higher-order structure and hydrogen bonding which plays an important role in stabilizing polymer structure [11].

2. Methods

PHB (Mn=1000), glycol chitosan with purity ≥ 60% and degree of deacetylation 91.6% [11] were purchased from Polysciences, Inc. and Sigma-Aldrich Co., respectively. They were used as received without any pre-treatments. The solvent of 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was received from Wako Pure Chemical Industries, Ltd. Film samples of PHB homopolymer and PHB/glycol chitosan with blending ratios of (80/20) and (60/40) were prepared by dissolved-casting method. Firstly, the powder of PHB and glycol chitosan were dissolved in HFIP at 60℃ based on the calculated weight percentages. After that, the mixture of the blends were discharged into aluminium dishes for evaporation process at 20℃ for 12h. The obtained film samples were then moved into vacuum oven and continued the evaporation at 70℃ for 12h in order to optimize the crystallization process.

THz spectra of the blend films were measured by using a terahertz time-domain spectrometer (THz-TDS), TAS7400TS from ADVANTEST Co. The spectra were obtained in the transmission mode in the 120–60cm$^{-1}$region with 1024 scans and 0.25cm$^{-1}$ spectral resolution. Temperature-dependent THz measurements were performed by attaching temperature control stage LINKAM 10002L in the THz-TDS spectrometer with the heating rate of 5 °C/min. The spectra were measured from 30℃ to melting temperature in every 5℃.

3. Results and discussion

![Figure 1 THz spectra of temperature dependent investigation of (a) PHB homopolymer (b) PHB/glycol chitosan (80/20) and (c) PHB/glycol chitosan (60/40).](image)
Figure 1 shows the THz spectra of PHB homopolymer and PHB/glycol chitosan for the blend ratios of (80/20) and (60/40) in the region of 110–70 cm\(^{-1}\) obtained during heating process from 30\(^\circ\)C to 145\(^\circ\)C for PHB homopolymer and from 30\(^\circ\)C to 140\(^\circ\)C for the PHB/glycol chitosan. The spectra at the lowest temperature (30\(^\circ\)C) reveal two clear peaks at 97 cm\(^{-1}\) and 82 cm\(^{-1}\) for PHB homopolymer and PHB/glycol chitosan (80/20) and the peaks at 95 cm\(^{-1}\) and 82 cm\(^{-1}\) for PHB/glycol chitosan (60/40). Those peaks of homopolymer PHB are related to the PHB-crystalline form and has been identified as spring like motion of helical structure due to the vibrational motion of CH\(_2^+\)CH\(_3\) out plane for the one at 97 cm\(^{-1}\), while the other one at 82 cm\(^{-1}\) was assigned to hydrogen bonding interaction of PHB due to the vibration of C=O and CH\(_3\) out plane [11].

In the 30\(^\circ\)C, PHB homopolymer shows the sharpest and highest absorbance of the peaks at 97 cm\(^{-1}\) and 82 cm\(^{-1}\) compare than other samples. It indicates that PHB homopolymer forms the higher-order structure and the presence of glycol chitosan can transform PHB into less-order structure.

The peak at 95 cm\(^{-1}\) of the PHB/glycol chitosan (60/40) has the lowest absorbance and it shows big absorbance ratio with the one at 82 cm\(^{-1}\). Since the peak at 95 cm\(^{-1}\) is related to the helical structure of PHB, the result indicating that PHB inside the PHB/glycol chitosan (60/40) system has the shortest helical structure. In this case, further investigation need be performed by wide angle X-ray scattering (SAXS) method to observe the lamella or helical structure thickness of PHB in the blend samples.

The film of PHB homopolymer and PHB/glycol chitosan blends were measured during heating process every 5\(^\circ\)C in order to understand the spectral behaviour. In Figure 1 (a), it is clear that the absorbance of PHB crystalline peak decrease during the heating process and finally disappear at 145\(^\circ\)C, in this stage PHB homopolymer is in molten stage or amorphous phase. Different with PHB/glycol chitosan (80/20) and (60,40), the peaks are still can be observed in the highest temperature even with the small absorbance. In another word, PHB still has the small helical structure and a very few hydrogen bonding. This indicates that glycol chitosan is able to inhibit transformation process of PHB from the crystalline state to the amorphous state.

Peak related to hydrogen bonding of PHB at 82 cm\(^{-1}\) shifts to higher wavenumber as temperature increases for all of the samples. This shifts mean that the hydrogen bonding of PHB weakens by heating process. Plots of the shifts are displayed in the Figure 2 (a), (b), and (c) for PHB homopolymer, PHB/glycol chitosan (80/20), and (60,40), respectively. In the low temperature from 30\(^\circ\)C to 80\(^\circ\)C, the 82 cm\(^{-1}\) peak of PHB homopolymer shifts gradually and the dramatically from 85\(^\circ\)C to 145\(^\circ\)C. In the case of PHB/glycol chitosan (80/20), the 82 cm\(^{-1}\) peak shifts gradually from 30\(^\circ\)C to 80\(^\circ\)C and it remains in almost same position from 85\(^\circ\)C to 140\(^\circ\)C. PHB/glycol chitosan (60/40) almost shows the same behaviour of PHB/glycol chitosan (80/20), the 82 cm\(^{-1}\) gradually shift in the low temperature and then remains in almost same position in the higher temperature. However, there is some difficulties to specify the peak positions due to extremely low absorbance.
4. Conclusion

PHB homopolymer and PHB/glycol chitosan with the blend-ratio of (80/20) and (60/40) have been investigated by THz spectroscopy to monitor the transformation in the higher-order structure and hydrogen bonding during heating process. THz spectra of PHB/glycol chitosan (80/20) and (60/40) have the same peaks as PHB homopolymer appear at 97 cm$^{-1}$ and 82 cm$^{-1}$ with slightly different position for the ratio at (60/40). The small peaks absorbance and the big peak ratios of the blend samples indicating that the presence of glycol chitosan in PHB homopolymer can transform the higher-order structure of PHB to the less-order. The hydrogen bonding of PHB homopolymer collapses in the high temperature yet it does not happen in the blend samples. Glycol chitosan can maintain the hydrogen bonding interaction of PHB even in its melting temperature.

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