RAMAN AND INFRARED STUDIES OF THERMAL BEHAVIOUR AND CRYSTALLINITY OF BIODEGRADABLE POLYHYDROXYALKANOATE

Rumi Murakami1*, Harumi Sato1, Fuminobu Hirose2, Kenichi Senda2, Isao Noda3, and Yukihiro Ozaki1

1School of Science and Technology, Kwansei Gakuin University, Sanda 669-1337, Japan
E-mail: scbc0122@ksc.kwansei.ac.jp
2Polymer Designing and Processing Research Laboratories, Kaneka Co. Settu 556-0072,
3The Procter and Gamble Company, 8611 Beckett Road, West Chester, Ohio 45069, USA

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Abstract: Raman and IR spectra of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); P(HB-co-HHx) and poly(3-hydroxybutyrate) (PHB) were measured over a temperature range of 20 • to near their melting points to explore their structure and thermal behaviour.

Poly(3-hydroxybutyrate) (PHB) and its copolymers, polyhydroxyalkanoate (PHA), are biologically synthesized polyesters produced by a number of microorganisms and are consequently subjected to degradation by bacteria in the soil. PHA are completely biodegradable under aerobic and anaerobic conditions and can be produced from renewable resources. Among all natural polymers, only PHA process thermoplasticity and mechanical properties similar to those of synthetic polymers. Since these polymers are biodegradable, they have receiving much attention as new environmentally friendly materials, and numerous industrial applications, including new medical applications, are explored [1], [2].

In the present study the thermal behaviour and crystallinity of poly(3-hydroxybutyrate); PHB and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); P(HB-co-HHx) (HHx=2.5, 3.4, and 12 mol %) were investigated by using IR and Raman spectroscopy [3]. Figure 1 compares chemical structures of PHB (A) and P(HB-co-HHx) (B). The temperature-dependent IR and Raman spectra have been analysed in detail in the C=O stretching, CH3 bending, and C-O-C stretching band regions, and bands characteristic of crystalline and amorphous parts were identified in each region. The PHB and P(HB-co-HHx) samples were dissolved in chloroform and then cast as a film by evaporating the solvent. The films were kept in a vacuum-dried oven at 60 • for 12 hours, and cooled down to room temperature.

Raman spectra were measured for films of PHB and P(HB-co-HHx) by using Kaiser HolProbe Raman spectrometer equipped with a CCD detector. An excitation wavelength at 785 nm was provided by a laser diode. The Raman dates were obtained at spectral resolution of 4 cm⁻¹.

Figure 1; Chemical structures of (A) poly(3-hydroxybutyrate) PHB and (B) poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) P(HB-co-HHx) (HHx=2.5, 3.4, and 12 mol%)
Figure 2 (A) displays Raman spectra in the C=O stretching band region of films of PHB and P(HB-co-HHx) (HHx=2.5, 3.4, and 12 mol %) at the room temperature. Of note in the comparison of the four spectra is that the relative intensity of the broad feature due to the amorphous parts increases with the increase in HHx content. This result is in a good agreement with the fact that the order of crystallinity is PHB, P(HB-co-HHx) (HHx=2.5 mol %), P(HB-co-HHx) (HHx=3.4 mol %), P(HB-co-HHx) (HHx=12 mol %). Another important point in the comparison is that the frequency of the crystalline C=O band is among the four kinds of PHA.

Figure 2 (B) shows IR spectra in the C=O stretching band region of films of PHB and P(HB-co-HHx) (HHx=2.5, 3.4, and 12 mol %) at the room temperature. As in the case of the Raman spectra, that the relative intensity of the broad feature due to the amorphous parts increases with the increase in HHx content.

It is noted that the spectral patterns of Raman and IR spectra obtained for the cast samples are similar to each other. The relative intensity of C=O stretching band centered at around 1740 cm\(^{-1}\) due to the amorphous parts increases with the increase in the HHx content. This result is in a good agreement with the fast that the order of crystallinity is PHB, P(HB-co-HHx) (HHx=2.5 mol %), P(HB-co-HHx) (HHx=3.4 mol %), P(HB-co-HHx) (HHx=12 mol %).

**References:**