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Spectral Characterization of Four Kinds of Biodegradable Plastics: Poly (Lactic Acid), Poly (Butylenes Adipate-Co-Terephthalate), Poly (Hydroxybutyrate-Co-Hydroxyvalerate) and Poly (Butylenes Succinate) with FTIR and Raman Spectroscopy

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Abstract Fourier transform infrared microscope and confocal Raman spectroscope were employed in this study to investigate four kinds of biodegradable plastics: poly(lactic acid),poly(butylenes adipate-co-terephthalate), poly(butylenes succinate) and poly(hydroxybutyrate-co-hydroxyvalerate), which are used more and more popularly in everyday life but can not be identified easily with other instruments. Infrared and Raman spectra of the plastics were tentatively interpreted. The indicative peaks to characterize the four polymers were also summarized. The result in this study can help the forensic scientists discriminate the plastics accurately when they occurred as trace evidences in cases, it also offers the producer and environment scientists an effective, non-invasive and fast method to characterize and identify these four polymers.

Keywords Fourier transform infrared spectroscopy · Confocal Raman spectroscopy · Biodegradable plastics

Introduction

Discarded synthetic plastics products induced serious problem of solid waste pollution, so many studies has been carried out on the biodegradable polymers which could offer an effective way to replace the commodity synthetic polymers and sovle the solid waste pollution in recent years [1, 2]. Poly(lactic acid) (PLA, Fig. 1(1)), poly(butylenes adipate-co-terephthalate) (PBAT, Fig. 1(2)), poly(butylenes succinate) (PBS, Fig. 1(3)) and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV, Fig. 1(4)) are four kinds of biodegradable plastics used most popularly in people's everyday lives.

Poly(lactic acid) is a thermoplastic aliphatic polyester derived from renewable resources which can easily be biodegraded under the presence of oxygen. Poly-L-lactide (PLLA) is the product used most popularly in everyday life among several distinct forms of PLAs. Poly-L-lactide has a crystallinity of around 37 %, a glass transition temperature between 60 and 65 °C, a melting temperature between 173 and 178 °C and a tensile modulus between 2.7–16 GPa [3]. PLA has good mechanical, thermal and biodegradable properties and therefore is a good polymer for various end-use applications. However, high brittleness and cost of PLA is the major problem for their commercialization and applications [4, 5]. PBAT is also a commercially available biodegradable plastics now widely used even worldwide. PBAT is an aliphatic-co-aromatic co-polyester synthesized by esterification of 1, 4-butanediol with aromatic dicarboxylic acid and then polycondensation with succinic acid. PBAT has many advantages among all the biodegradable materials, including high flexibility, excellent impact strength and melt processibility. In particularly PBAT has very fast biodegradation rate. It is reported that whether in the form of films or molded objects, PBAT has exhibited significant biodegradation within 1 year in soil, water with activated sludge, and seawater [6–9]. PBS is another biodegradable aliphatic polyester produced by the polycondensation reaction of 1,4-butanediol with succinic acid [10, 11] It has high flexibility, excellent impact

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Fig. 1 Chemical structures of
PLA (*1*), PBAT (*2*), PBS (*3*)
and PHBV (*4*)
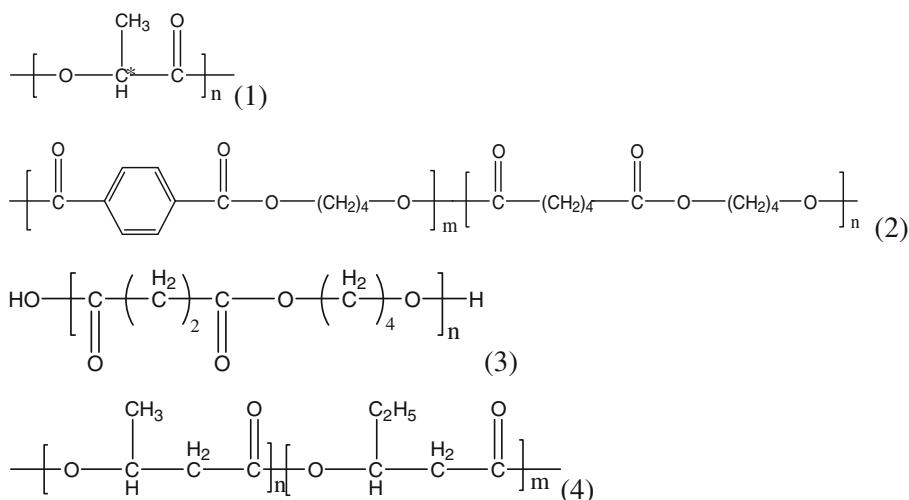
strength, and thermal and chemical resistance [12]. PBS can be processed easily. Many studies on PBS have indicated that PBS can easily be biodegraded within several months in the envrionment [5]. PHBV is another promising biopolymers known as polyhydroxy alkanoates (PHAs) that can be produced via bacterial fermentation of plant starches. PHBV has gained special importance because of favorable mechanical characteristics, biological properties, highly adaptable structure, non-toxic degradation products, and minimal inflammatory response when used as scaffold, PHBV is also found with fast degradation rate in the envrionment in the previous studies [13].

It is important to characterize the platics in relative studies, especially in the research on synthesis and envrionmental degration progress. Thermal analysis, X-ray diffraction, Nuclear magnetic resonance (NMR) and spectroscopy such as scanning electronic microscopy-energy disperse spectroscopy are all ideal methods to characterize these biodegradable plastics. However, previous studies only focused on the characterization of mechanical (tensile and impact) properties, thermal properties, rheological properties, morphology and biodegradability in the synthesis and production research [14–18]. IR characterization was also involved in some previous studies, but peak assignment of the fuction groups was not systemic and detailed enough. To our best of knowledge, few studies on fast and noninvasive characterization of these four kinds of plastics with Raman, IR and Raman in combination were found. FTIR spectroscopy had been proved to be an effective tool with many advantages in the characterization of plastics [19, 20]. Very few sample was needed for anlysis and high-quality spectra could be obtained only in a few seconds. Raman spectroscopy aslo requires only small sample volumes and minimal sample

preparation, the analysis is fast and accurate. Raman spectroscopy can cover the shortage of FTIR spectroscopy(such as serious water interference) and give extra structure information. More structure information would be obtained if these two methods used in combination, and optical observation with these two methods were performed in the study to investigate the spectral characteristics.

Materials and Methods

Four kinds of biodegradable plastics samples were kindly presented by the National Technical Commitee on Plastic Products of Standardization Administration of China. A Spectrum GX 2000 system from Perkin-Elmer Company with diamond anvil cell, DTGS (Deuterated triglycine sulfate) detector and Spectra 5.01 workstation was employed for IR investigation. Background was subtracted for every measurement. Triplicate tests were performed at different sites for every sample.

A Renishaw invia confocal Raman microscope system with two lasers emitting at 532 nm/633 nm, charge-coupled device (CCD) detector was employed collecting the Raman spectrum. 532 nm laser was chosen for emission in 10–100 % power depending on whether the laser would damage the sample or not. Before every sample measurement, crystal silicon with fixed peak position at 520 cm^{-1} was used to calibrate the Raman shifts. The spectra were collected in WIRE3 workstation in extensive mode ranging from 100 to 3,200 cm^{-1}. For some samples, most peaks appeared in the bands of 150–2,000 cm^{-1}, so 2,000–3,200 cm^{-1} were not shown in this study and the spectrum in 150–2,000 cm^{-1} was magnified to get better

Fig. 2 IR spectrum of PLA
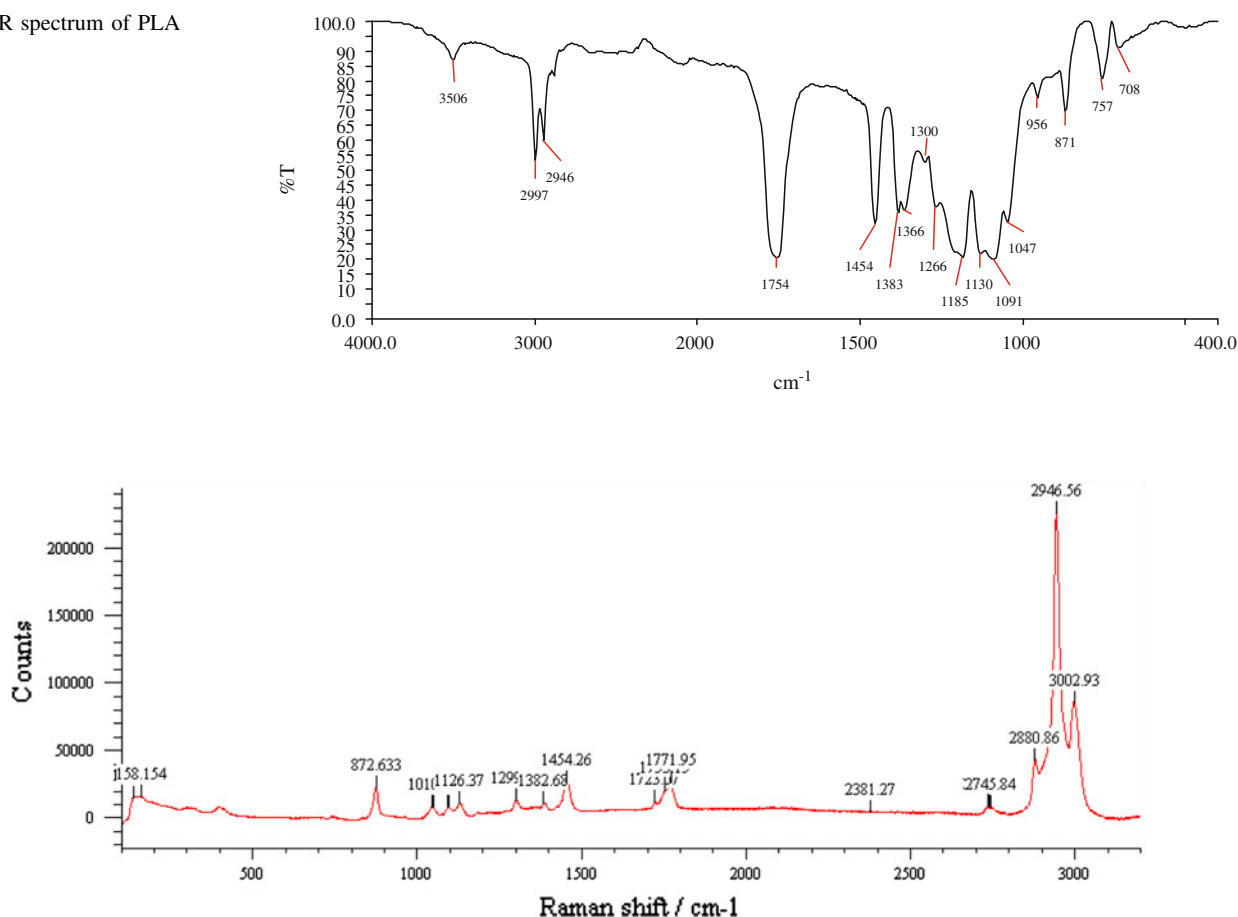
Fig. 3 Raman spectrum of PLA

spectrum. Every spectrum was obtained by 3–15 accumulations to enhance the signal/noise ratio.

Results and Discussion

Spectrum of PLA

Figures 2 and 3 showed the IR and Raman spectra of PLA separately. Sixteen peaks: 3,506, 2,997, 2,946, 1,754, 1,454, 1,383, 1,366, 1,300, 1,185, 1,130, 1,091, 1,047, 956, 871, 757, 708 cm^{-1} were identified in the IR spectra of PLA. More specifically, 3,065 cm^{-1} should be assigned as the OH absorption in stretching mode; 2,997, 2,946 cm^{-1} CH$_3$ stretching mode; CH$_3$ stretching band was increased by the inductive effect of the adjoining C = O or O atom. 1,754 cm^{-1} was the absorption of C = O stretching which was increased from about 1,730 cm^{-1} by the hyper conjugation of α-H and the C = O. 1,454 cm^{-1} was the asymmetric bending absorption of CH$_3$; 1,383, 1,365 cm^{-1} should be assigned as the symmetric bending absorption of CH$_3$, CH;1,266, 1,185, 1,130, 1,091, 1,047 cm^{-1} were all

stretching absorption of C–O–C which were complex because of the different atoms of function groups adjoining to C–O–C;870 cm^{-1} should be assigned as the absorption of O–CH–CH$_3$ and 757 cm^{-1} as the wagging absorption of α-CH$_3$. The OH absorption at 3,506 cm^{-1}, the shift of C = O stretching mode from 1,730 to 1,754 cm^{-1} and the wagging absorption of α-CH$_3$ at 757 cm^{-1} were all characteristic and indicative in the identification of PLA.

IR and Raman spectroscopy can give more information by using these two instruments in combination. Some C–C or C = C absorption, especially strong absorption of C = C in benzene ring(1,620 cm^{-1}), appeared in Raman spectrum but dispeared in IR spectrum; while some absorption of polar function groups appeared in IR spectrum but disppeared in Raman spectrum. It indicated that Raman spectrum has fewer and less overlapped bands than in the infrared spectrum. Many peaks appeared at similar possitions in IR and Raman, so they were not further interepted in Raman spectrum. From Figs. 2 and 3, C = O stretching was observed at both IR (1,754 cm^{-1}) and Raman (1,772 cm^{-1}) spectrum. 315, 401, 873, 1,010, 1,096, 1,126, 1,299, 1,383, 1,454, 1,723, 1,772, 2,746,

Fig. 4 IR spectrum of PBAT
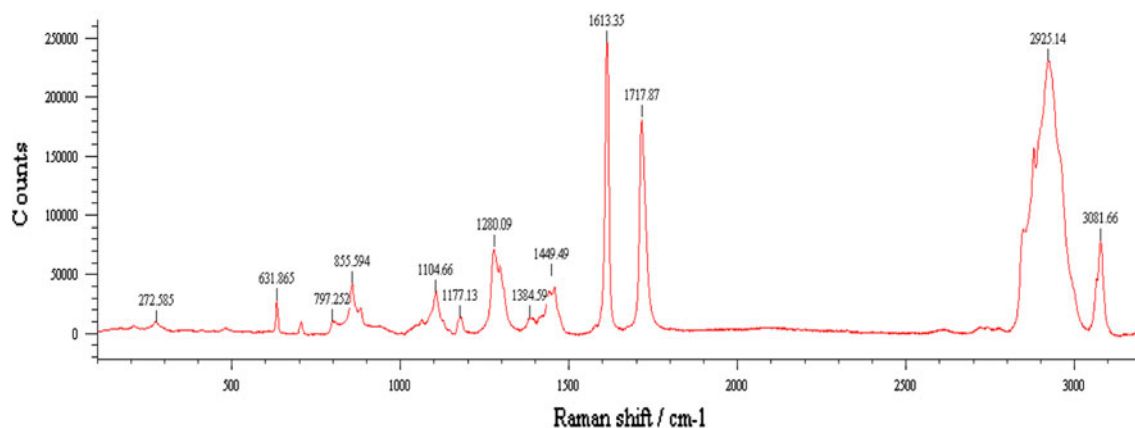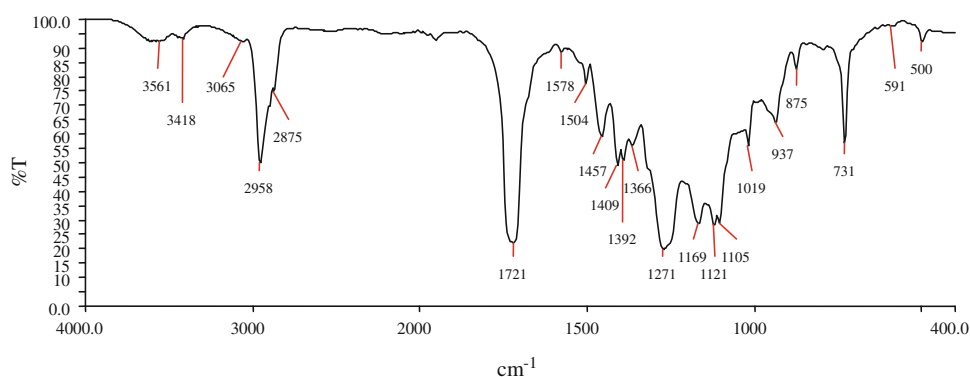
Fig. 5 Raman spectrum of PBAT

2,881, 2,947 and 3,003 cm^{-1} were the main peaks in the Raman spectrum of PLA.

Spectrum of PBAT

Main IR peaks of PBAT were 3,065, 2,958, 2,875, 1,392, 1,366, 1,169, 1,121 and 937 cm^{-1} from Fig. 4. 3,065 cm^{-1} in PBAT should be assigned as the =C–H absorption in stretching mode; 2,958, 2,875 cm^{-1} CH$_3$, CH$_2$ stretching mode; 1,578, 1,504 cm^{-1} skeleton vibration of benzene ring; 1,457 cm^{-1} CH$_2$ in-plane bending mode; 1,409 cm^{-1} bending mode of O–CH$_2$; 1,366 cm^{-1} out-plane bending mode of CH$_2$; 1,271, 1,105 cm^{-1} C–O stretching mode; 1,019 cm^{-1} in-plane bending mode of =C–H in benzene ring; 875, 731 cm^{-1} should be assigned as out-plane bending mode of =C–H in benzene ring and 850 cm^{-1} as in-plane bending mode of CH$_2$. The out-plane bending mode of =C–H in benzene ring generally appeared in 830 cm^{-1}, but influenced by the conjugation of C=O and the benzene ring, the absorption occurred in 731 cm^{-1} was characteristic in the spectrum and were found to be indicative in the identification of PBAT. From the difference in the structures and spectra of PBAT and PET, 1,121,

1,169 cm^{-1} should be assigned as the stretching mode of the C–O in alphabetic acid. Peaks at 731, 1,121 and 1,169 cm^{-1} were characteristic and can be used as indicative peaks in the identification of PBAT.

From Fig. 5, the main peaks in the Raman spectrum of PBAT included: 119, 206, 273, 632, 704, 797, 856, 878, 1,024, 1,043, 1,105, 1,177, 1,280, 1,300, 1,396, 1,449, 1,577, 1,613, 1,673 and 1,718 cm^{-1}. The peaks at 2,003, 2,760, 2,780, 2,782, 2,875, 3,045 and 3,067 cm^{-1} were also found in the Raman spectrum of PBAT in the magnified spectrum, considering these peaks were not characteristic enough, they were not labeled in Fig. 5.

Spectrum of PBS

Figure 6 showed the IR spectrum of PBS. From Figs. 1(3) and 6, peaks in the IR spectrum of PBS should be assigned as following: 2,965, 2,948, 2,859 cm^{-1}, CH$_3$, CH$_2$ stretching mode;1,722 cm^{-1}, C=O stretching mode;1,159 cm^{-1}, C–O stretching mode;1,046 cm^{-1}, O(CH$_2$)$_4$ O vibration;955 cm^{-1},C–O symmetric stretching mode;806 cm^{-1}, CH$_2$ in OC(CH$_2$)$_2$CO in-plane bending mode and 654 cm^{-1}, COO bending mode. Peaks at 955, 806 and

Fig. 6 IR spectrum of PBS
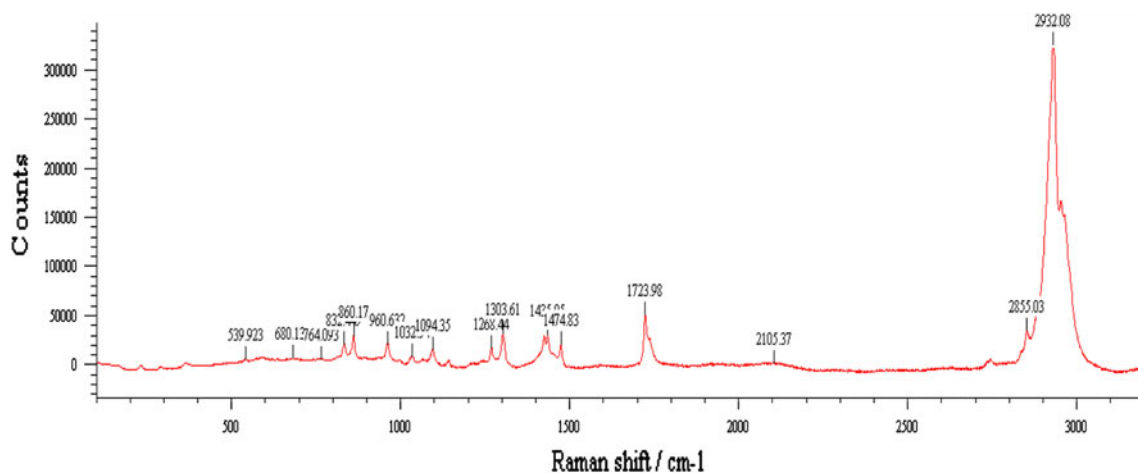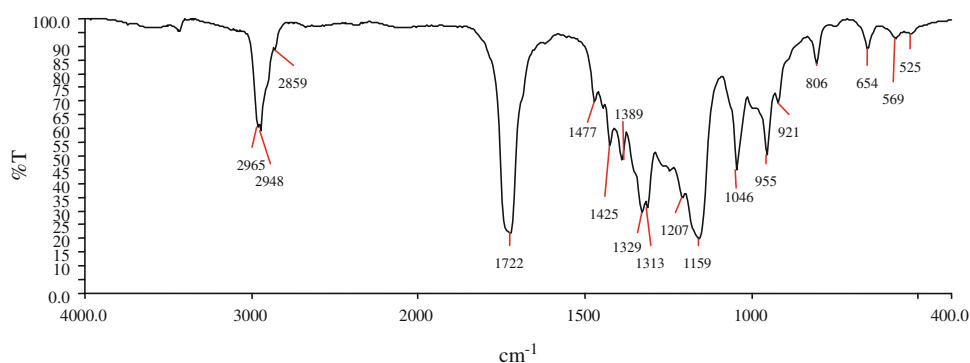
Fig. 7 Raman spectrum of PBS

654 cm^{-1} can be used as indicative peaks to discriminate PBS to other kinds of plastics. From Fig. 7, the main peaks in the Raman spectrum of PBS were 838, 860, 961, 1,032, 1,094, 1,268,1,304, 1,425,1,475, 1,724, 2,855 and 2,932 cm^{-1}.

Spectrum of PHBV

IR spectrum of PHBV (3HB-co-3H) was shown in Fig. 8. From the chemical structure of PHBV in Figs. 1(4) and 8, Peaks in IR spectrum of PHBV should be assigned as: 3,612 cm^{-1}, OH stretching mode; 2,977, 2,935, 2,879 cm^{-1}, CH_2, CH_3 stretching mode; 1,728 cm^{-1}, C = O stretching mode; 1,454 cm^{-1}, CH_2 bending mode; 1,380 and 1,358 cm^{-1}, CH_3 bending mode; 1,300–1,000 cm^{-1}, C–O–C stretching mode and 980 cm^{-1}, CH_2 in-plane bending mode. Peaks at 1,000–1,300 cm^{-1} in fingerprint bands and 980 cm^{-1} will be helpful in PHBV identification. From Fig. 9, the main peaks in the Raman spectrum of PHBV in 100–2,000 cm^{-1} were:217, 289, 366, 432, 597, 697, 836, 910,953, 1,056, 1,100, 1,131, 1,216, 1,250, 1,294, 1,361, 1,401, 1,453, 1,604 and 1,726 cm^{-1}.

It was easy to discriminate the Raman spectrum of PBAT from PLA, PBS and PHBV. From Fig. 1, there were C = O and benzene rings structures in the PBAT chains while there were only C = O structures in the other three polymers. So, the Raman shifts relative to the benzene rings only appeared in the spectrum of PBAT. Specifically, the peak at 3,082 cm^{-1} was the absorption of the unsaturated = C–H; 1,613 cm^{-1} might be assigned as the absorption of the C–C stretching in the benzene ring; 1,280 cm^{-1} as the C–C stretching and the –C–CH in-plane bending in the benzene ring; 1,105 cm^{-1} as the –C–CH in-plane bending and 856, 797 cm^{-1} as the –C–CH out-plane bending. The intense peaks at 1,613 and 3,082 cm^{-1} were helpful in the identification of PBAT. The super conjugation effect of the α-H and the C = O in the PLA shift the stretching vibration of C = O to 1,772 cm^{-1}. It was significantly higher than those in the other compounds with C = O including PBS (1,724 cm^{-1}) and PHBV (1,726 cm^{-1}), so it could be used as a indicative peak of PLA. Intense peaks at 860 and 961 cm^{-1} appeared in the spectrum of PBS but did not appear in that of PHBV, so PBS and PHBV could be discriminated with the two peaks effectively.

Fig. 8 IR spectrum of PHBV
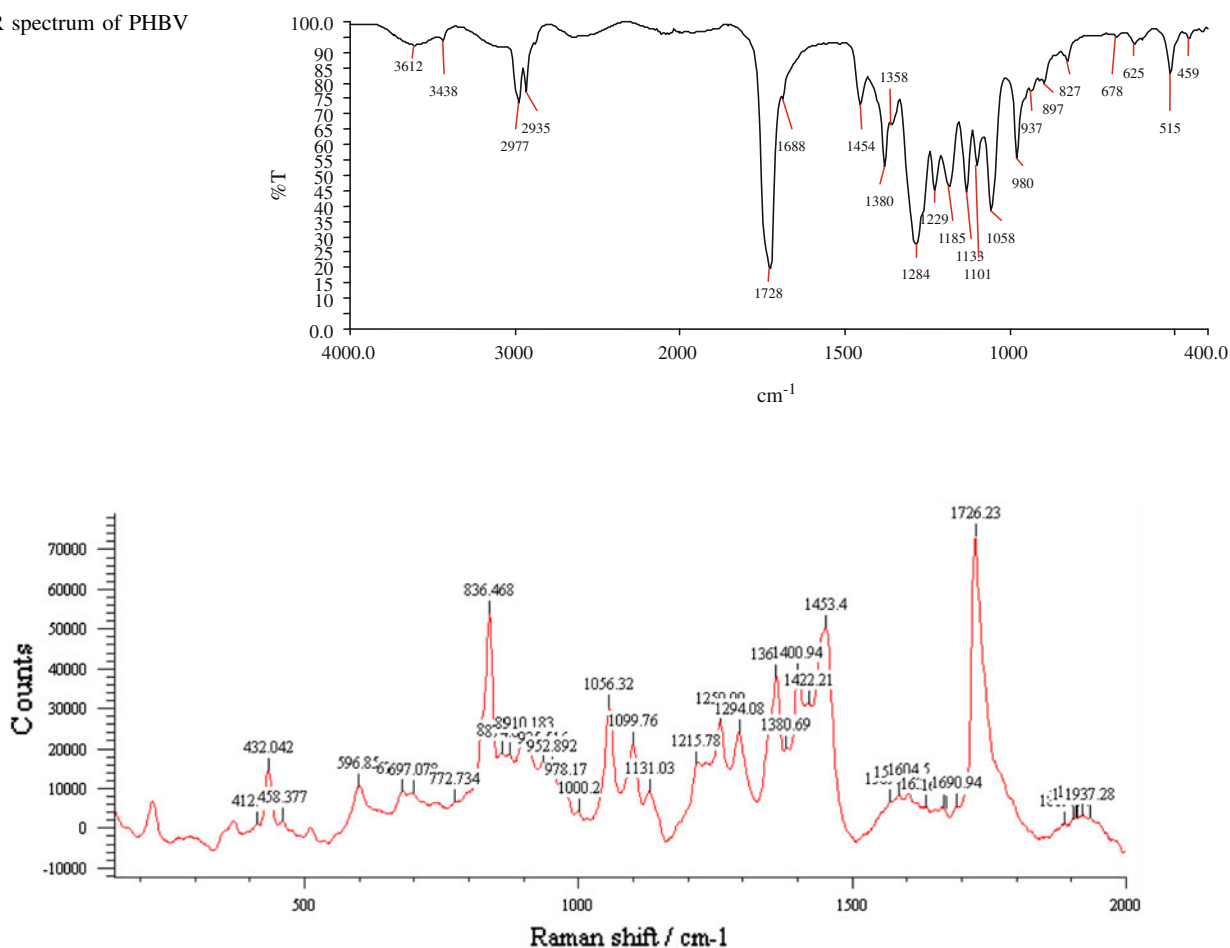
Fig. 9 Raman spectrum of PHBV

In conclusion, four kinds of biodegradable plastics: PLA, PBAT, PBS and PHBV were collected and examined for spectral characterization in this study. Peak positions were investigated. Main peaks in the spectra were also tentatively assigned to corresponding function groups. Peaks of the OH absorption at 3,506 cm^{-1}, the shift of C = O stretching mode from 1,730 to 1,754 cm^{-1} and the wagging absorption of α-CH$_3$ at 757 cm^{-1}; peaks at 731, 1,121 and 1,169 cm^{-1}; peaks at 955, 806 and 654 cm^{-1} and peaks at 1,000–1,300 cm^{-1} in fingerprint bands and 980 cm^{-1} were found to be indicative in the identification of PLA, PBAT, PBS and PHBV in IR spectrum separately. The characterization would be more accurate with the complementary information from IR and Raman spectroscopy and the method proved to be an effective, non-invasive and fast method to characterize and identify these four polymers.

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