Polymer Testing 57 (2017) 52–57

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material Characterisation

Characterizing polymorphism and crystal transformation of polylactide by terahertz time-domain spectroscopy

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ARTICLE INFO

Article history:
Received 20 May 2016
Received in revised form
14 August 2016
Accepted 11 November 2016
Available online 12 November 2016

Keywords:
Terahertz time-domain spectroscopy
Polylactide
Crystal transformation
Stereocomplex

ABSTRACT

Terahertz time-domain spectroscopy (THz-TDS), which has been proved to show promising application in complex polymer systems, was employed to investigate the polymorphism phenomenon and crystal transformation of polylactide (PLA) in this study. The THz-TDS shows sensitive response on the crystal structure. The α′-form, α-form and stereocomplex crystals exhibit absorption peaks of lattice vibration at 1.82, 2.01 and 2.09 THz, respectively. THz-TDS has no direct chirality identification on the difference between poly (D-lactide) (PDLA) and poly(L-lactide) (PLLA). However, the PLA stereocomplex shows an extra and distinctive absorption peak at 1.43 THz compared with homo-PLA, and the peak was proved to be stemmed from the collective vibration of L-lactic unit and D-lactic unit pairs connecting by hydrogen bonds. This is the first time that THz-TDS has been proved to be of great potential in identification of polymer stereocomplex crystal. Also, the α′→α crystal transformation of PLA were intuitively investigated at 120 °C using THz-TDS, while the transformation rate was quite slow.

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1. Introduction

The recent rapid development of spectroscopic techniques in the terahertz (THz) frequency range has enabled the facile investigation of molecular vibrations in the frequency range of 0.1–3.0 THz [1,2]. This newly risen method can probe physical phenomena including low-energy excitations and carrier dynamics in electronic materials, collective vibrational or torsional modes in condensed-phase media, and rotational and vibrational transitions in molecules [3,4]. Thus, THz spectroscopy has recently received great attention with the expectation that it will provide new insights into complex polymer systems (such as glass transition, skeletal vibrations, side-chain vibration and the libration of hydrogen bond, etc.), and several relevant studies have been reported [5–17]. For example, Hoshina et al. had assigned the THz absorption peaks at 2.49 and 2.92 THz of poly(3-hydroxybutyrate) (PHB) to the vibrations due to the intermolecular hydrogen bonding and helical structure along the fiber axis, respectively [13,14]. Furthermore, they revealed that the C–H···O=C hydrogen bonds are initially formed before establishment of well-defined crystal structures using THz two-dimensional correlation spectroscopy [15]. Suzuki et al. showed that THz spectroscopy is a powerful method for investigating polymorphism phenomenon and crystal transformation of nylon-6 and found a new anomaly at 110 °C [16]. Therefore, THz spectroscopy is of great potential in studying crystallization behavior of semi-crystalline polymers.

Polylactide (PLA) is one of the bio-based and biocompatible polymers expected to be alternative to petroleum-based polymers. It is well known that PLA has three kinds of steric configurations including poly(L-lactide) (PLLA), poly(D-lactide) (PDLA) and poly(D,L-lactide) (PDLLA) regarding to the polymerization enantiomorphism isomeric monomers. Among them, the PLLA and PDLA are thermoplastic crystalline polymers whose degree of crystallinity can be as high as 60%, while PDLLA is an amorphous polymer. More attractive is that the crystalline PLA exhibits polymorphism phenomenon and can crystallize into various crystal forms under different conditions, such as α-form, α′-form (δ-form), β-form and γ-form [18–21]. The most common two and easy acquired crystal forms are α-form and α′-form. The α-form crystal can be easily prepared from melt and solution crystallization process. In particular the chains in α-form adopt 10_3 helix conformation and pack into an orthorhombic lattice [18,22]. When isothermally crystallized below 120 °C from melt, PLA forms the α′-form crystal. α- and α′-forms coexist once PLA melt crystallizes

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http://dx.doi.org/10.1016/j.polymertesting.2016.11.017
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at the temperature range between 100 and 120 °C [23,24]. The α′-form comprises the same 10_3 helix yet with delicate different but loose in later packing. However, recently study by Su et al. indicated that the intrinsically metastable α′-form crystals can partially transform into α-form crystals at 80 °C through a continuously increasing packing density process [25]. The β-form crystal shows a melting temperature about 10 K lower than α-form crystal [23] and can be obtained by stretching the melt or solution spun fibers from the stable α-form crystal at very high draw ratio and high temperature [22]. Recently, Lotz has presented that the PLLA α′-form results from a crystal-crystal transformation from a parent but very transient β-crystal phase, and the β-phase displays the characteristic single crystal diffraction pattern of frustrated polymers [26].

In addition to the homo-crystallization of PLA, a stereocomplex (SC) crystal forms from equimolar mixture of PLLA and PDLA in both melts and solutions due to the strong interaction between L-lactic segments and D-lactic segments compared with that between L-lactic segments or D-lactic segments [27–29]. The SC crystal possesses a melting point of 220–230 °C, which is about 50 K higher than that of PLLA or PDLA homo-crystal, and it shows significantly improvement of crystallization capability compared with homo-PLA [30]. Cartier et al. suggested that the SC crystal should be described as a trigonal frustrated unit cell, in which PLLA chains take on left-handed 3_1 helical conformations and PDLA chains form right-handed 3_1 helices [31]. Moreover, hydrogen bonds have been proved to exist in forms of $CH_3\cdots O{=}C$ and $C_\alpha H \ldots O{=}C$ in SC crystal [32–35], while there only van der Waals force and dipole–dipole interaction exist in homo-PLA crystal [36]. The denser packing condition and formation of hydrogen bonds between PLLA and PDLA chains cause the higher melting point of the complex.

In this work, we measured the THz absorption spectra of homo-PLA in various polymorphs (α′-form crystal, α-form crystal and their blend) and PLA stereocomplex. The results revealed that THz spectrum is an effective method to distinguish PLA crystal structure, to investigate the $\alpha' \rightarrow \alpha$ crystal transformation and to identify the chiral stereocomplex crystal.

2. Experimental section

2.1. Materials

PLLA pellets (trade name 4032D) were purchased from NatureWorks® LLC (USA), the weight-average molecular weight (M_w) is 2.49 × 10^5 g/mol. PDLA, PDLLA, L-lactide (L-LA) and D-lactide (D-LA) were purchased from Ji'nan Daigang Biological Engineering Company (China). The M_w of PDLA and PDLLA are 2.30 × 10^5 g/mol and 1.90 × 10^5 g/mol, respectively. All dissolved reagent were analysis grade and used as received.

2.2. Sample preparation

PLLA and PDLA were first dried in a vacuum oven for 24 h at 60 °C before using. PLLA and PDLA were dissolved in chloroform respectively with a concentration of 0.02 g/mL and stored at room temperature. Then films of PLLA/PDLA blends with different weight ratios (*i.e.*, 3:1, 2:1, 1:1, 1:2, 1:3) were prepared by casting mixed solution of PLLA and PDLA into glass Petri dishes. The mixed solution was stirred for 1 h before casting, and the solvent was allowed to evaporate at room temperature (~25 °C) for 12 h. Later, the resulting films were dried for another 24 h in vacuum oven at 60 °C to remove the residual solvent.

Sandwiched between two glass slides, PLLA, PDLA and PLLA/PDLA blends were placed on a hot stage (WT-2010, Shanghai Weitu Company, China) at a fixed temperature (30 K above the melting point) to melt. The thickness of the sample was controlled at about 180 μm. After melting for 3 min, the sample was quickly transferred onto another hot stage (Linkam THMS600, United Kingdom) preset at the required isothermal crystallization temperature for a specific time. Finally, the sample was quenched to room temperature and the glass slides were gently removed to obtained free-standing film for further characterization.

2.3. X-ray diffraction

Wide angle X-ray diffraction (WAXD) measurements of the samples were carried out on a D8 Advanced Bruker instrument (Germany) with Cu K_α radiation source ($\lambda_{Cu} = 0.154$ nm). Data were collected in the 2θ interval from 5° to 40° with a scanning rate of 2°/min and the scanning step was 0.02°.

2.4. Terahertz time-domain spectroscopy (THz-TDS)

A standard a THz-TDS setup (Fig. 1, A mode-locked Ti: sapphire laser with a central wavelength of 800 nm, pulse duration of 100 fs, and repetition rate of 80 MHz is used as the optical source.) based on photoconductive switches are used to characterize the THz transmission spectra of samples and reference, the detailed information on their system and data process has been reported in the previous work [37,38]. The samples were measured at ambient temperature in a dry nitrogen atmosphere at 25 °C. Each sample or reference was tested six times to reduce random noise, and six time-domain data were averaged to improve the SNR. Then the sample and reference amplitude spectra were obtained from the averaged time-domain data by Fourier transform and denoted as $A_s(\omega)$ and $A_r(\omega)$, respectively. The amplitude absorbance ($\alpha(\omega)$) spectra were obtained by the equation:

$$\alpha(\omega) = -\ln\left(\frac{A_s(\omega)}{A_r(\omega)}\right)$$

3. Result and discussion

3.1. THz-TDS spectra of homo-PLA crystals

Fig. 2a presents the WAXD diffractograms of PLLA isothermally crystallized at various temperatures in the range of 80–130 °C. The

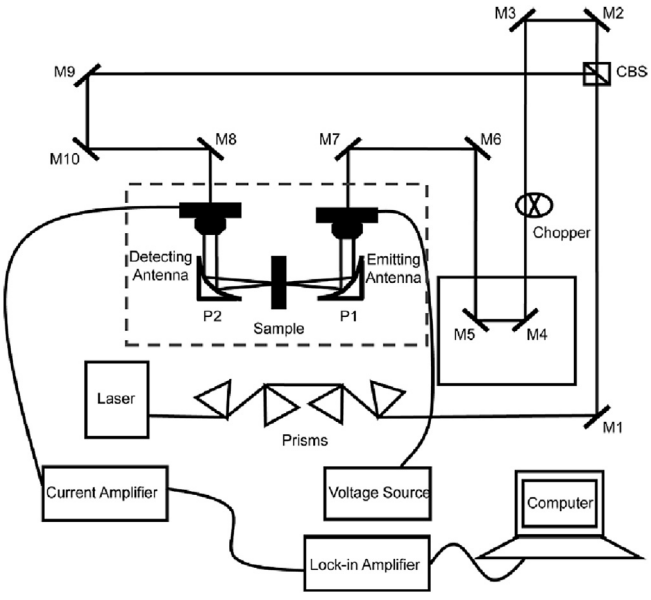

Fig. 1. The sketch of THz-TDS setup.

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