



The effect of poly(vinyl phenol) sublayer on the crystallization and melting behavior of poly(3-hydroxybutyrate) via hydrogen bonds



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ABSTRACT

The cold crystallization and melting behavior of poly(3-hydroxybutyrate)(PHB) layer on amorphous Poly(vinyl phenol) (PVPh) and Si wafer substrate were studied by using Grazing incidence X-ray diffraction and infrared reflection-absorption spectroscopy. Compared to the PHB on Si wafer, the PVPh layer shows great influence on the crystallization and melting behavior of PHB layer. The depression extent of melting temperature increases with the increase of PVPh thickness when the thickness of PVPh is smaller than a critical value. Infrared reflection-absorption spectroscopy study is carried out to better understand the structure evolution of PHB and its interaction with PVPh in the heating process. By monitoring and decomposing the C=O stretching bands, several points can be identified: (1) melting temperature decreases with PVPh thickening; (2) the fraction of intermolecular hydrogen bonds formed between the OH groups of PVPh and C=O groups of PHB is very small below glass transition temperature of PVPh and it increases significantly above 100 °C. Moreover the fraction increases with PVPh thickness. The effect of PVPh thickness on the formation of hydrogen bonds is attributed to the roughness, molecular mobility and/or molecular orientation of PVPh.

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1. Introduction

Due to the rapid development of coating, adhesion, nanoscience and nanotechnology, the design and fabrication of ultrathin polymer layers are of increasing importance. The macromolecular structures in the confined geometry play an important role on the final properties of ultrathin films. Therefore, the structure characterization and understanding the impact of nanoconfinement on the structure of polymer thin films have drawn intense interest.

Much attention has been focused on glassy polymers and in particular on the glassy-state structure relaxation near surface and interface. There is now substantial evidence that nanoconfinement effect on the *glass transition temperature* (T_g) is related to surface and interface [1–5]. The length scale at which confined glassy structure relaxation deviates from bulk T_g ranges from tens of nanometers (<100 nm) in the absence of attractive substrate interface to values exceeding 100 nm in the presence of strongly

attractive substrate interaction [5]. Therefore, a distribution of T_g exists in the confined polymer thin films. Taking the PMMA supported on a silica substrate, the substrate and free surface affect the structural relaxation rate over similar distance and the distribution in relaxation rate extends to at least 100 nm but less than 250 nm.

The crystallization of polymers in the confined two dimensional geometry has also received considerable attention in recent years due to most of synthetic polymers are semicrystalline materials. Although crystallization of polymer chains follows the conventional habit whereby polymer chains fold back and forth to form crystalline lamellae, the crystallization kinetics including nucleation and crystal growth can be profoundly affected by nanoscale confinement [6–15]. The alteration of crystallization kinetics may be attributed to the change in the T_g and/or molecular mobility of polymer chains in confined nanofilms. Besides crystals kinetics, lamellar orientation is also changed significantly under spatial confinements. The preference of lamellar orientation is determined by the film thickness [16–23], crystallization temperature and substrate surface energy [7,8,24–28]. Moreover, the melting behavior of polymer crystals in thin film is also known to be significantly affected by film thickness and the interaction between polymer film and substrate [29,30]. The melting temperature

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decreases with the decrease of film thickness when the film is thinner than a certain critical thickness, and the magnitude of the depression increases with increasing surface interaction.

The above referred studies on the deviation from bulk of the thermal properties in the nanoconfined geometries have greatly extended and deepened our knowledge on the origin of this nanoconfinement. However, predominant substrates supporting nanofilms are solid substrates such as Si wafer rather than soft materials. Recently, due to technical interests in the filed of all-polymer optical devices filter membranes and drug delivery systems, polymer–polymer interface is frequently involved. The polymer structure at the interface and the related properties profoundly regulate the overall performance of multilayer film materials. Therefore, probing the thermal properties of a polymer layer on another kind of soft polymer layer is the potential rewards both in the terms of providing new evidence to better understand the nature of the thermal properties of nanoconfined thin film and developing new technologies for enhanced film performances.

Poly(3-hydroxybutyrate) (PHB) is a natural and biodegradable polyester found in bacteria as an energy storage system as small granules within the cell. The crystalline structure of PHB consists of an orthorhombic system $P2_12_12_1-D_2^4$ with $a = 5.76 \text{ \AA}$, $b = 13.20 \text{ \AA}$, and $c = 5.96 \text{ \AA}$ (fiber repeat) [31]. Because of its similar thermal and mechanical properties to isotactic polypropylene and potential application in the field of agricultural, marine and medical application, PHB has attracted more and more attention. However, there are a few problems which limit its industrial application greatly. For example, PHB is rigid and stiff because of the high crystallinity. Decreasing the crystallinity of PHB is one of the ways to increase its practical value. Therefore, the approach of blending has been used to improve the properties of PHB. Many hydroxyl group containing polymers, such as poly(vinyl phenol) (PVPh), are good counter polymer to be mixed with PHB, because those blends have been found form miscible systems driven by the intermolecular hydrogen bonding interaction [32–34]. For the PHB/PVPh blend system, Xing reported that this blend system is miscible at all compositions by analyzing the T_g and equilibrium melting point [34]. Recently, Ozaki et al. advance the investigation of this system further by using IR and XRD [35,36]. They decompose the vibration spectra in the C=O stretching region into three fundamental vibration spectra. The first one is *inter* C=O (between the C=O groups and the OH groups in the PVPh). The second one is the *intra* C=O (between the C=O group and one of the C–H groups in CH_3 side groups of PHB chains). The third one is the free C=O groups of PHB in amorphous phase or melt. They explore the thermally induced exchanges of various kinds of hydrogen bonding interactions in the heating process. PHB chains and PVPh chains are incorporated in polymer networks formed by physical cross-linking points. The fraction of *inter* C=O increases with the weight fraction of PVPh. Both crystallization and melting of the blends occur in the following two step processes. The crystallization involves the dissociation of intermolecular hydrogen bonds, followed by the transformation of *inter* C=O to *intra* C=O within lamellae. While melting involves the dissociation of *intra* PHB, followed by the transformation of the dissociated free C=O into *inter*.

In the present study, the poly(vinyl phenol) (PVPh), an amorphous polymer, is selected to help decreasing the crystallinity of PHB. The nanolayer assemblies of PHB/PVPh on Si wafer were prepared and the effect of PVPh substrate on the crystallization and melting behavior of PHB layer is compared with that of the Si wafer. A depression of the crystallinity and melting temperature is observed on the PVPh substrate and the magnitude of the depression enlarges with the thickening of PVPh layer. The hydrogen bonding formed between the OH group of PVPh and C=O group of PHB occurring at the interface of PVPh and PHB is

monitored. And its relation with the crystallization of PHB and its thickness dependence are also explored.

2. Experiment

Bacterially produced PHB with a weight-averaged molecular weight of $6.0 \times 10^5 \text{ g mol}^{-1}$ was obtained from the Procter & Gamble Co. To remove any impurities, the polymer was dissolved in hot chloroform, precipitated in methanol, and vacuum-dried at $60 \text{ }^\circ\text{C}$. Next, 0.8% (m/v) PHB solutions in chloroform were spin-coated onto two different types of substrates at a rotating speed of 4000 rpm at room temperature. One type of the substrate is Si (100) wafer, which was cleaned in water using ultrasonic waves before use. The Si (100) wafer surface is covered by tens of nanometers thick SiO_2 . The other type is Si wafer covered with a PVPh layer which was prepared by spin-coating the PVPh tetrahydrofuran solution onto silicon wafers and then dried in a vacuum oven at $130 \text{ }^\circ\text{C}$ for 6 h. PVPh with the glass transition temperature at around $106 \text{ }^\circ\text{C}$ was purchased from Aldrich Co. It should be noted that the PVPh sublayer will not be destroyed during the process of spin-coating of PHB as the PVPh substrate cannot be dissolved by chloroform. The obtained PHB/Si and PHB/PVPh/Si samples were put in vacuum oven ($20 \text{ }^\circ\text{C}$) for one week to erase the residual solvent before measurement. The samples were heated at a heating rate of $2 \text{ }^\circ\text{C}/\text{min}$ and allowed to equilibrate for 15 min before the collection of data.

2.1. IR measurement

Infrared reflection-absorption spectroscopy (IR-RAS) with a 2 cm^{-1} resolution using a Thermo Nicolet NEXUS 870 FTIR spectrometer with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector was used to measure the spectra of PHB and PVPh in the heating process. A total of 128 scans were co-added for each IR spectral measurement to ensure a high signal-to-noise ratio.

2.2. X-ray measurement

The thicknesses and roughness of the PVPh sublayer were determined by fitting X-ray reflectivity (XR) data using an in-house developed software that used a recursive method based on the dynamical scattering theory (See Supporting Information in Fig. S1). The T_g of PVPh is determined by the PVPh thickness dependence on temperature. X-ray diffraction was used to characterize the crystallization status and crystal structure of PHB. Grazing incidence X-ray diffraction (GIXD) measurements were conducted on a high-resolution four-circle diffractometer with a rotating-anode X-ray generator (SLX-2000&UltraX, Rigaku Co., Ltd., X-ray wavelength = 0.15405 nm). The size of the incident beam was defined by a 2 mm-diameter collimator. A Soller slit was placed before a scintillation detector to collimate the scattered beam. The GIXD measurements were performed with in-plane and out-of-plane configurations, in order to detect crystalline structures perpendicular and parallel to the substrate surface, respectively. The fixing time for data collection was 50 s per step, and the angular interval was 0.01° and 0.05° for out-of-plane and in-plane profiles, respectively.

3. Results

3.1. Crystallization and melting behavior of PHB thin films on Si wafers

Fig. 1a shows the temperature dependence of the out-of-plane X-ray diffraction profiles of a 45 nm-thick PHB film placed on Si

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