

TEMPERATURE-DRIVEN SURFACE MORPHOLOGY EVOLUTION OF POLY(3-HYDROXYBUTYRATE) SINGLE LAYER AND POLY(3-HYDROXYBUTYRATE)/POLY(VINYL PHENOL) BILAYER ON Si WAFERS*

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Abstract The specular and off-specular X-ray reflectivities were efficiently employed to study the evolution of surface morphology as a function of temperature in a single layer of poly(3-hydroxybutyrate) (PHB) and a bilayer of PHB/poly(vinyl phenol) (PVPh) on Si substrates. The results indicate that the changes of thickness and surface roughness caused by pre-melting of PHB crystals are not obvious for the single layer, whereas the surface roughness of the PHB layer and the intensity of the off-specular X-ray reflectivity for the bilayer exhibit a remarkable non-monotonic change in the temperature range of 100–150°C; the roughness parameter evaluated by the specular X-ray reflectivity reaches its maximum at 120°C. The interaction at the interface between PVPh and PHB certainly contributes to the non-monotonic changes. Such interaction also affects the crystallization and melting behavior of PHB thin film greatly. The crystallization of PHB thin film is inhibited even on the glassy surface of PVPh sublayer. In the melting process, the PHB crystals on PVPh sublayer feature a three-section melting curve separated by a plateau region of 120–140°C.

Keywords: Interface; Hydrogen-bond; Roughness; Melt.

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INTRODUCTION

Polymer thin films play an essential role in many commercial application fields, such as coating, adhesive, packing and resist. The modification and properties of macromolecular chains in the confined 2D geometry behave differently from those in the bulk due to the existence of free surface and interface. Understanding on the molecular process occurring at the interfaces is, therefore, increasingly important for a wide range of researchers.

The system for a single layer of crystalline and amorphous polymers on a solid substrate has been extensively studied. For a crystalline polymer layer on a solid substrate of nucleation type the crystal growth rate and crystal orientation are very sensitive to the buried interface and free surface^[1–12]. In addition, the melting behaviors of the crystalline polymer layers are also known to be significantly affected by the interaction between

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the polymer and substrate^[13, 14]. For an amorphous polymer on a solid substrate, the glass transition temperature (T_g) and dewetting behavior have been the two main research directions. There is strong evidence that the interaction between the substrate and polymer layer plays a crucial role in determining the direction of the T_g shift. An increase in T_g is generally observed when the interaction is strong, whereas a depression in T_g occurs if the interaction is weak^[15–19]. The dewetting behavior of polymers on solid substrates has also drawn extensive attention. The wetting to dewetting transition depends on the nature and strength of the interaction between the polymer layer and substrate^[20–26].

Compared with the commonly studied single layer system, the stability and homogeneity of stacked two polymer layers on solid substrates require much more complicated discussion. Such kind of two-layers allows richer dynamics than the single-layer system during heating process, because the complex interfaces evolve in a coupled way. The evolution is driven by the effective molecular interactions between all of the interfaces separating the four materials: solid substrate, two polymeric component layers and ambient gas. Several studies have been carried out on the incompatible double-layered polymer systems, and the values of the interfacial width between the polymer layers as functions of film thickness, molecular weight and annealing temperature are determined^[27–34]. By comparing the experimentally obtained interfacial widths with the values predicted by the self-consistent field theory, the existence of capillary wave is identified, which leads to an increase of the interfacial width in many cases^[31–37]. The stability of the layered films of two immiscible polymers and the dewetting dynamics of such systems depend mainly on the relative viscosities of the two liquids, the thicknesses of the respective liquid layers, as well as the surface and interfacial tensions^[38–43].

Although a number of studies have focused on different aspects of double-layered polymer systems, those of crystalline/amorphous double polymer layers have rarely been studied. This is actually of great interest, as a great amount of crystalline polymer is involved in the field of all-polymer optical devices, filter membranes and drug delivering systems. The evolution of molecular structure at the interfaces profoundly regulates the overall performance of multilayer polymer materials.

Grazing-angle X-ray is a powerful technique to characterize the structure of thin polymer films. The combination of different surface scattering methods like specular X-ray reflectivity (XRR) and off-specular XRR, which is the diffuse scattering component adjacent to specular XRR, can help to distinguish different structural evolutions occurring in quasi-2D systems. In specular XRR, the intensity of the reflected X-ray beam is measured as a function of grazing incidence angle with equal incoming and outgoing grazing angles (Fig. 1a). The average electron density of each layer or electron density profile as functions of distance z from the sample surface, surface roughness, interface roughness, and thickness of each layer can be obtained through the analysis based on the dynamical scattering theory. However, the information obtained by specular XRR is laterally-averaged information at a depth of z from the sample surface. Statistical feature on lateral fluctuation characterized by two-body correlation function as a function of distance $R = (x^2 + y^2)^{1/2}$ like lateral

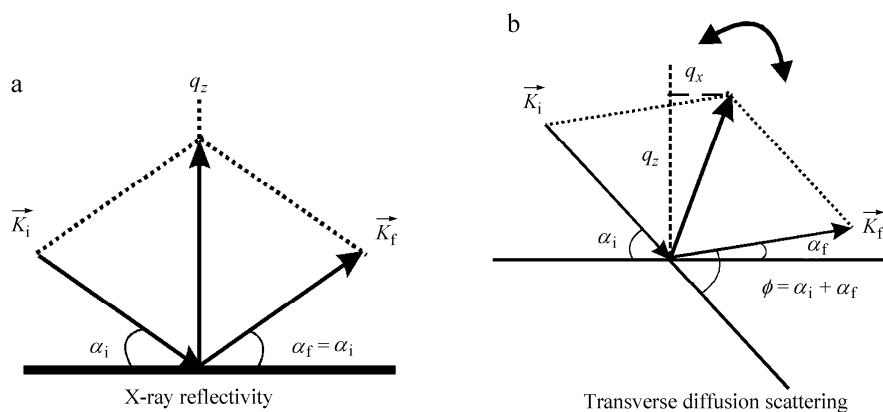


Fig. 1 Schematic representation of (a) specular and (b) off-specular X-ray reflectivity

inhomogeneities of surface and interfaces can be obtained by employing the diffuse off-specular XRR. A measurement of off-specular XRR for detecting the signature of capillary waves can be performed by the “transverse scan along q_x ” (q_x scan). The scattering geometry of q_x scan is illustrated in Fig. 1(b). Under this geometry, the sum of the incidence (α_i) and exit (α_f) angles is fixed. Here, the in-plane component of the scattering vector q_x varies while the component perpendicular to the surface q_z keeps constant. Here, the incoming and outgoing X-ray are $\vec{K}_i$ and $\vec{K}_f$, respectively.

In the present study, we select poly(3-hydroxybutyrate) (PHB) as the capping layer and amorphous poly(vinyl phenol) (PVPh) as the buried layer on Si substrate, *i.e.*, a PHB/PVPh/Si kind sandwich structure, to reveal the evolutions of molecular structure different from those of PHB/Si system using the technique of X-ray diffraction and XRR. It was well documented that PHB and PVPh compose a miscible blend system. The specular and off-specular XRR results indicate that the roughness of PHB layer on the surface of PVPh thin film exhibits a non-monotonic change above the T_g of PVPh. By contrast, the roughness of a similar PHB layer directly on Si wafer does not change significantly. Such kind of substrate-dependent roughness change has not been observed by other techniques. Moreover the crystallization of PHB thin film is inhibited even on the glassy surface of PVPh sublayer. In the melting process, the PHB crystals on PVPh sublayer feature a three-section melting curve separated by a plateau region of 120–140°C.

EXPERIMENTAL

Bacterially produced PHB with a weight-averaged molecular weight of 6.0×10^5 was obtained from the Procter & Gamble Co. To remove impurities, the received polymer was dissolved in hot chloroform, precipitated in methanol and then vacuum-dried at 60°C. The PVPh with T_g at around 104°C was purchased from Aldrich Co. and used as received. To make PVPh covered Si wafer, a uniform thin PVPh layer was spin-coated from its tetrahydrofuran solution with a concentration of 0.5 wt% onto Si wafer and then dried in a vacuum oven at 130°C for 6 h. The spin-coating was performed at room temperature with a rotating speed of 4000–4500 r/min. Thin layers of PHB were spin-coated from its 0.4 wt% chloroform solution either onto the Si wafer, which has been cleaned in water using ultrasonic waves, or onto the PVPh covered Si wafer, which creates a PHB/PVPh/Si kind sandwich structure. It should be noted that, during the spin-coating process of PHB layer onto PVPh surface, the morphology of the PVPh layer on Si is not disturbed since PVPh could hardly be dissolved by chloroform. The obtained PHB/Si and PHB/PVPh/Si samples were measured using the surface-sensitive grazing incidence X-ray diffraction techniques.

Specular and off-specular XRR measurements were conducted using a high-resolution four-circle diffractometer equipped with a rotating-anode X-ray generator (SLX-2000&UltraX, Rigaku Co., Ltd., $\lambda = 0.15405$ nm). The size of the incident beam was defined by a collimator with 0.2 mm in diameter. A Soler slit with the width of 0.1 mm and height of 5 mm was placed before a scintillation detector to collimate the scattered beam. The reflected intensity was accumulated for 50 s per step and the angular interval in the scanning was 0.01°. The thicknesses of the polymer thin films deposited on the Si wafers were determined by fitting the specular XRR profiles using an in-house developed software that uses a recursive method based on the dynamical scattering theory^[44]. Transverse scans along q_x were carried out at a fixed q_z value ($q_z = 1.17 \text{ nm}^{-1}$); the fixing time and angular interval for off-specular XRR data collection are the same as those in the specular XRR.

RESULTS

The PHB Thin Film on Si Wafer

Figure 2(a) shows the temperature dependence of X-ray diffraction for a 45.6 nm-thick PHB film on Si wafer. The normalized peak area of (020) reflection is displayed in Fig. 2(b). One can see that as the temperature increases, the intensity of (020) reflection shows an increase up to 80°C and a nearly constant intensity in the range of 80–140°C followed by a smooth drop. The crystals of PHB melt completely at 165°C.

Figure 3 depicts the plots of specular XRR for a 45.6 nm-thick PHB film during a heating process on a Si

wafer substrate. The solid curves show the fitted results. The best fitting parameters including thickness, roughness of free surface ($\sigma_{\text{air/PHB}}$), roughness of interface ($\sigma_{\text{PHB/Si}}$), electron density of PHB (ρ_{PHB}) are listed in Table 1. From Fig. 3, it can be seen that the profile did not change significantly in the temperature range of 25–160°C except for a slight decrease in the amplitude of Kiessig fringes. Considering that the average electron density of polymer layer and the roughness parameters are correlated in the least-squares fittings and both of them contribute to the change in the amplitude of Kiessig fringes, it is reasonable to have an image that the ρ_{PHB} decreases a little bit and/or the $\sigma_{\text{air/PHB}}$ increases slightly in this temperature range. Taking into account that 50% PHB crystals melt at 160°C, one can realize that the pre-melting of crystalline PHB film only leads to a slight change in ρ_{PHB} and $\sigma_{\text{air/PHB}}$. After complete melting of PHB crystals at 165°C, the Kiessig fringe becomes very fuzzy and even disappears at 170°C. The absence of Kiessig fringe can be attributed to the increased roughness caused by the melting of PHB crystals.

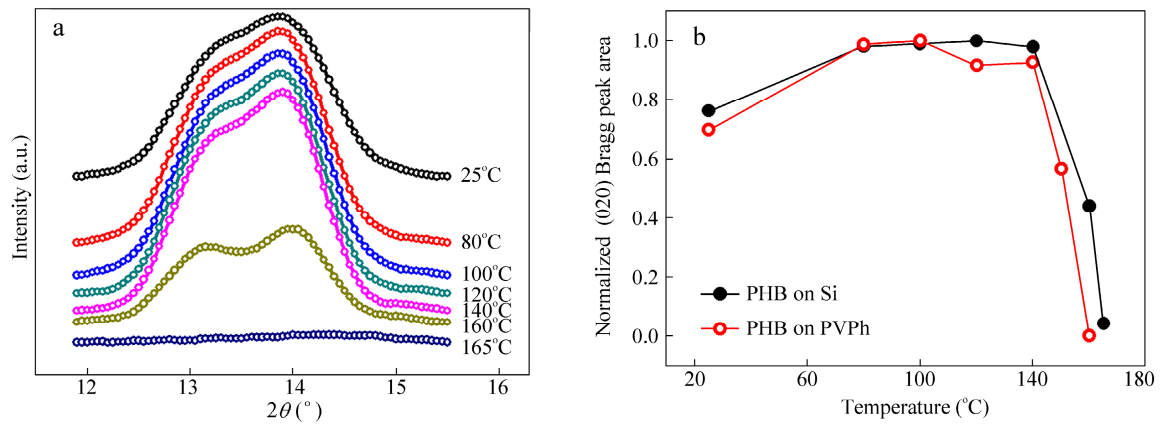


Fig. 2 X-ray diffraction profiles for PHB thin film on Si substrate (a) and the normalized (020) peak intensity of PHB thin films on Si and PVPh sublayer as a function of temperature (b)

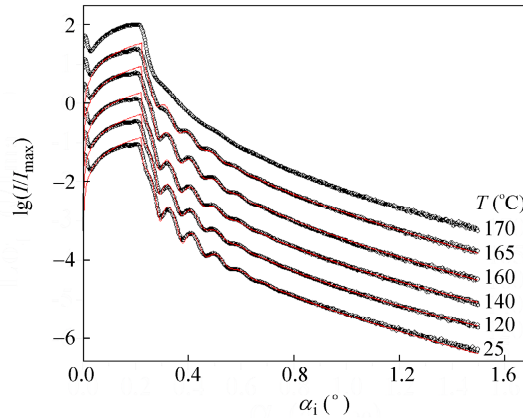


Fig. 3 Specular XRR (symbols) and fit (line) of a $d \approx 45$ nm PHB film deposited on a Si wafer at different temperatures (°C)
The curves are shifted on the intensity scale for clarity.

Table 1. Data obtained from the two-box model fitting for the PHB/Si XRR results

Temperature (°C)	25	80	120	140	150	160	165
$\rho_{\text{PHB}} \times 10^{-3} \text{ (nm}^{-3}\text{)}$	0.365	0.359	0.361	0.356	0.351	0.342	0.321
$h_{\text{PHB}} \text{ (nm)}$	45.54	45.69	45.33	45.39	45.61	45.86	46.79
$\sigma_{\text{air/PHB}} \text{ (nm)}$	3.0	3.0	3.2	3.1	3.0	3.1	3.4
$\sigma_{\text{PHB/Si}} \text{ (nm)}$	0.5	0.5	0.5	0.5	0.5	0.5	0.5

ρ : electron density of material; h : film thickness; σ : roughness

As specular reflectivity gives an averaged picture of surface morphology, more insight into the structure in the lateral direction can be provided by analyzing the diffuse scattering data. Figure 4 shows the experimental transverse scan data taken during a heating process at $q_z = 1.17 \text{ nm}^{-1}$. Three different characteristic regions can be recognized: the region where the incoming or outgoing X-ray evanescently propagates (region 1), the off-specular XRR region (region 2) and the region indicating the rocking curve of specular XRR (region 3)^[45]. In the region 1, dynamical effect dominates the scattering phenomenon. The pronounced maxima of the scattering intensity in region 1, which are referred to as the Yoneda peaks, are observed^[46]. The Yoneda peak is observed whenever the critical angle of total reflection (α_c) is equal to the incident angle (α_i) or the reflected angle (α_r). For example, at room temperature the Yoneda peak appears at the position of $\alpha_i = 0.17^\circ$ corresponding to the critical angle of PHB ($\alpha_{c\text{PHB}}$). The position of the another Yoneda peak locating at 0.21° is the same as the critical angle of the bare Si wafer ($\alpha_{c\text{Si}}$). In region 2, the scattered intensity consists mainly of the off-specular XRR. From the statistical information on the surface morphology along the lateral directions, more precise properties of material surface can be identified. Region 3 mainly provides the specular scattering. In the present study, we will focus on the analysis of region 2 coupled with region 1 to obtain additional structural information.

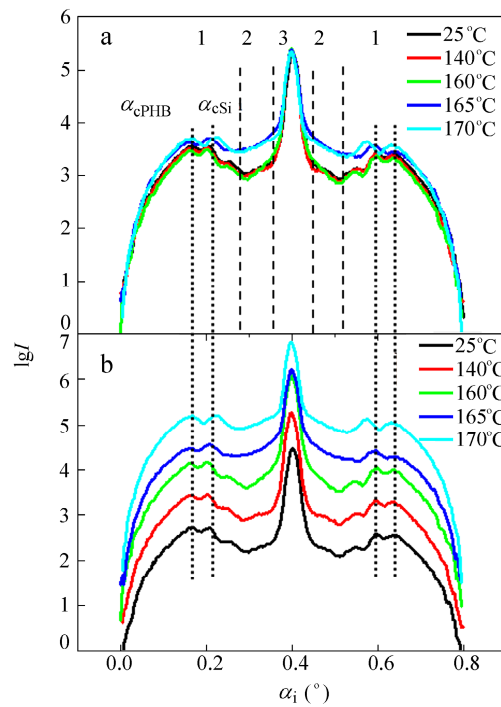


Fig. 4 Off-specular scans along q_x ($q_z = 1.17 \text{ nm}^{-1}$) for a PHB film on Si wafer as a function of temperature (a), and the shifted curves on the intensity scale (b)

To highlight the q_x -dependence of off-specular XRR in region 2, Fig. 5 depicts the lg-lg plots of the right-hand part of the curves shown in Fig. 4. In the temperature window of 25–160°C, the curve features with one peak and one broad hump, as indicated by the oval and arrows, respectively. At higher temperatures, *e.g.* 165°C and 170°C, the peak disappears and a characteristic power-law behavior is observed.

After viewing the evolution of the diffuse scatterings, two points can be discussed: (i) the peaks indicated by the oval are observable at relatively low temperatures while disappear along with the melting of the PHB crystals (165°C). Hence, the presence of this peak is most probably related with the crystallites distributed in the surface region. By calculating the length value corresponding to this peak (at $q_x = 10^{-2.83} \text{ nm}^{-1}$) which is around $4.2 \text{ }\mu\text{m}$, it can be speculated that distribution of crystalline domains yields some short-range orders with

characteristic length of several μm in the polymer film. The speculation can be proved by the AFM image which displays the presence of domains with the size around 3–8 μm on the surface of PHB films (see Fig. 6). (ii) Since the T_g of PHB is almost 0°C , the capillary wave should be present on the surface of PHB films. The optical microscopy observations prove the presence of capillary waves (See Fig. S1 in Supporting Information). The broad hump as indicated by the arrows, therefore, can be attributed to the lower cut of capillary wave (q_{lc})^[45, 47, 48]. The power-law region is very narrow due to the presence of crystalline domains peaked in the oval region. After the melting of PHB crystals (165°C and 170°C), the power-law region becomes quite clear. However, the q_{lc} is difficult to be discerned which presumably associates with the increase of capillary wave length or the decrease in film viscosity. The shift of peak position with increasing temperature (the arrows in Fig. 5) supports such speculation.

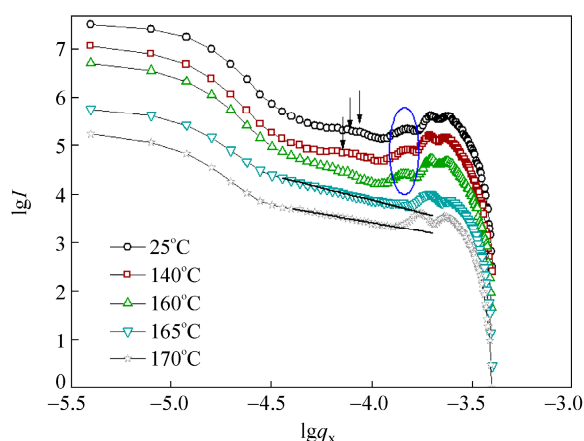


Fig. 5 lg-lg plots of the transverse diffuse scattering of the PHB/Si versus q_x for $q_z = 1.17 \text{ nm}^{-1}$. The curves are shifted on the intensity scale for clarity.

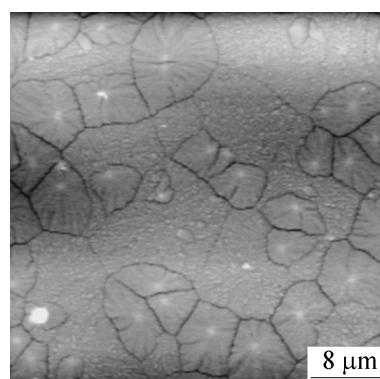


Fig. 6 An AFM image of a PHB thin film surface on Si substrate

The PHB/PVPh Double Layers on Si Wafer

Figure 7 shows X-ray diffraction of a 40.3 nm-thick PHB film on a 22.5 nm-thick PVPh sublayer. The normalized peak area of (020) reflection is displayed in Fig. 2(b). The crystallization of PHB on PVPh and Si sublayers exhibits the same magnitude of the peak intensity increment in the range of $25\text{--}80^\circ\text{C}$. However, the absolute (020) peak area of PHB on the PVPh substrate is much smaller than that on the Si wafer suggesting the crystalline degree of PHB is depressed significantly by PVPh substrate. Additionally, the peak shapes of (020) are very different and the two resolved peaks located at 13° and 14.2° are not observed on the PVPh substrate. In the melting process, the PHB crystals on the PVPh sublayer show a lower melting temperature. The melting of PHB on the 22.5 nm thick PVPh substrate takes place at 120°C (10% dropping down) followed by a plateau stage (120°C to 140°C) and a 90% peak intensity dropping down is found in the range of 140°C to 160°C . From the above observation, one can realize that the change of substrate from Si wafer to PVPh sublayer not only alters the crystallization behavior of PHB including the crystalline degree and crystal axial length thickness distribution, but also fascinates the melting process of PHB crystals. The lower crystallization degree and fast melting process can be attributed to the interaction occurring at the interface of PVPh and PHB which will be discussed as follows.

Figure 8 shows the specular XRR of the PHB film on the PVPh layer deposited on Si. It should be noted here that the thickness of the buried PVPh layer can be obtained separately before capping the PHB layer (PVPh in Fig. 8). The best fitting parameters including thickness, roughness of free surface, roughness of interface, electron density of the two polymer layers are listed in Table 2. Three-box model is employed when the temperature is lower than 140°C . At 25°C , the Kiessig fringes with the short period of 62.8 nm seen in the smaller q_z area must correspond to the total thickness of the PHB/PVPh double layers. The other type of obscure

Kiessig fringes with the period of 22.5 nm indicated by the arrows is observed at the larger q_z area. As the thickness is quite similar to that of neat PVPh layer, it can be stated that these Kiessig fringes come from the interference of reflected X-ray between the interface of PHB/PVPh and PVPh/Si. This phenomenon is very interesting as the reflected X-ray from the interface of polymer/polymer is barely observed due to the small electron density difference between PHB and PVPh. In the heating process, the interference pattern in specular XRR is very similar within the range of 25–100°C except for the slight shift of Kiessig fringe to the right direction, indicating the film thickness decreased a little bit.

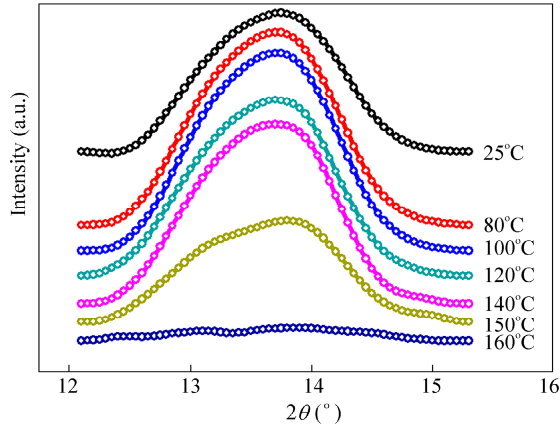


Fig. 7 X-ray diffraction profiles for PHB thin film on PVPh sublayer

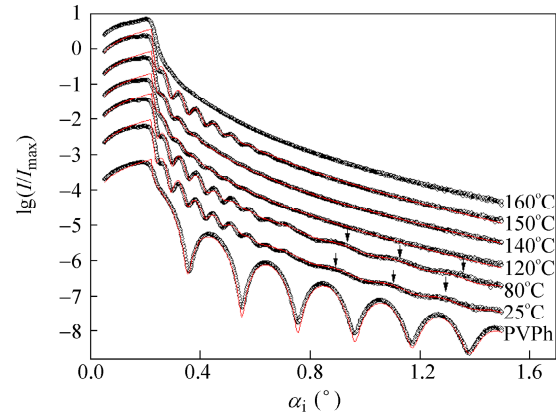


Fig. 8 XRR (symbols) and fit (line) of a $d \approx 40$ nm PHB film deposited on a $d \approx 22$ nm PVPh film as a function of temperature
The XRR of the neat PVPh layer before PHB capping is also shown (the bottom profile). The curves are shifted on the intensity scale for clarity.

Table 2. Data obtained from the two- and three-box model fittings for the PHB/PVPh/Si XRR results

	Three-box		Two-box			
Temperature (°C)	25	80	120	140	150	185
$\rho_{\text{PHB}} \times 10^{-3} \text{ (nm}^{-3}\text{)}$	0.359	0.370				
$\rho_{\text{PVPh}} \times 10^{-3} \text{ (nm}^{-3}\text{)}$	0.345	0.360	0.356	0.371	0.347	0.316
$h_{\text{PHB}} \text{ (nm)}$	40.36	39.95				
$h_{\text{PVPh}} \text{ (nm)}$	22.50	22.10	63.31	62.48	62.39	16.35
$\sigma_{\text{air/PHB}} \text{ (nm)}$	3.5	3.7	5.5	5.3	3.5	2.6
$\sigma_{\text{PHB/PVPh}} \text{ (nm)}$	0.2	0.2		–		
$\sigma_{\text{PVPh/Si}} \text{ (nm)}$	0.5	0.5	0.5	0.5	0.5	0.5

ρ : electron density of material; h : film thickness; σ : roughness

A remarkable change is evidenced at 120°C and the Kiessig fringes in the relatively smaller q_z area suddenly become very fuzzy, revealing a significant increase in the surface roughness. Moreover, the disappearance of the Kiessig fringes in the larger q_z area is an excellent indicator for the changes at the PHB/PVPh interface. Such kind of situation remains till 140°C. With further increase of temperature, the amplitude of Kiessig fringes in the smaller q_z area increases gradually. At 150°C, the observed specular XRR looks like the one obtained at 25°C except for the absence of Kiessig fringes in the larger q_z range. Taking the fact into account that the T_g of PVPh sublayer is 104°C, the decrease and subsequent increase in the amplitude of the Kiessig fringes in the temperature range between 120°C and 150°C may be related with the change of PVPh molecular mobility. The precise description for the change of film structure in this temperature range will be discussed later. At 160°C, the Kiessig fringes in the whole area completely disappear. The evolution of the specular XRR of PHB/PVPh on Si is thus quite different from that of a single PHB layer on Si. The variation of

the specular XRR patterns of the former one should be closely associated with the PVPh interlayer.

Measurements of off-specular XRR are also carried out to understand the morphological change of PHB layer on the soft-sublayer of PVPh (see Fig. 9). The lg- $\lg$ plots of the right-hand part of the curves shown in Fig. 9 are depicted in Fig. 10 highlighting the off-specular XRR region (region 2). From Fig. 10, it can be seen that the intensity curve features with one peak and one broad hump in the temperature window of 25–150°C, as indicated by the oval and arrows, respectively. Comparing with the results for the PHB thin film on Si (Fig. 5), one can realize that the positions of the peaks and broad humps do not change so much with the presence of PVPh layer. This suggests that the PVPh sublayer does not strongly affect the crystal domain size of PHB crystallites, neither the capillary wave length on the PHB surface. The off-specular profiles do not change much in the temperature window of 25–150°C, and the peak located at $q_x = 10^{-2.83} \text{ nm}^{-1}$ disappears at 160°C. The temperature at which the peak disappears is slightly lower than that of PHB/Si (at 165°C) suggesting that the PHB crystals are less stable on PVPh than that on Si. The lower melting temperature of PHB on PVPh is also proved by the Bragg diffraction data (Fig. 2b). At higher temperatures, *e.g.* 165°C a characteristic power-law behavior is observed suggesting the development of capillary wave.

To further clarify whether some variation of surface morphology of PHB/PVPh bilayer in such temperature window occurs, the off-specular profile in region 1 is analyzed. From Fig. 9(a), it can be seen that the shape of the Yoneda peak located in region 1 does not change too much at first (from 25°C to 100°C). The intensity increases from 100°C to 140°C followed by a clear decrease at 150°C. The non-monotonic change in Yoneda peak intensity is similar to the change in the amplitude of Kiessig fringes in the specular XRR profiles as both of them are sensitive to the change of roughness.

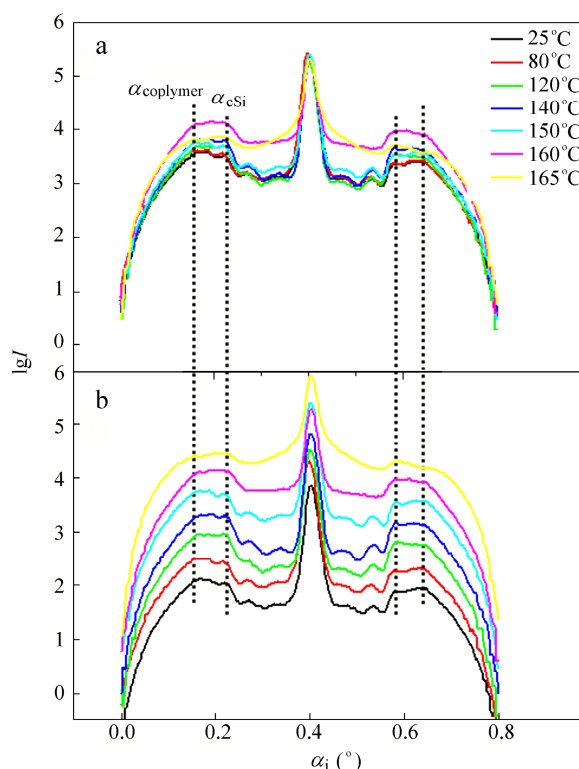


Fig. 9 Off-specular XRR along q_x ($q_z = 1.17 \text{ nm}^{-1}$) for the PHB/PVPh film at different temperatures on Si wafer (a) and the shifted curves on the intensity scale (b)

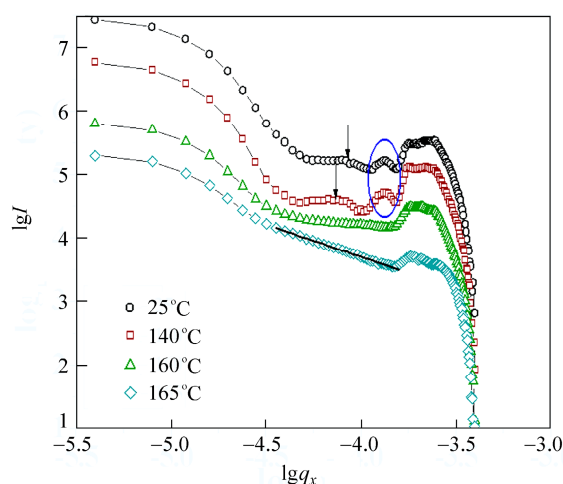


Fig. 10 lg-lg plots of the transverse diffuse scattering of the PHB/PVPh on Si versus q_x for $q_z = 1.17 \text{ nm}^{-1}$. The curves are shifted on the intensity scale for clarity.

DISCUSSION

From the combined analyses of X-ray diffraction, specular XRR and off-specular XRR, it can be found that the evolution of the PHB thin film on solid Si substrate during the heating process is very different from that on the PVPh substrate. The discussion can be separated to two parts: (1) A non-monotonic change in roughness and diffuse scatterings recognized in the temperature window of 100–150°C for the sample of PHB/PVPh; (2) The effect of PVPh substrate on the recrystallization and melting behavior of PHB.

Non-monotonic Change of Free Surface Roughness of the PHB/PVPh

The above description of the experimental results reveals that neither the specular XRR nor the off-specular XRR shows remarkable variation for the PHB/Si before the melting of crystalline PHB (below 165°C). In contrast, the PHB/PVPh bilayer exhibits an interesting non-monotonic change of the specular XRR and Yoneda peak intensity in the temperature range above T_g of PVPh and below the melting temperature of PHB (120°C to 150°C). The changes in surface roughness of the PHB/PVPh bilayer obtained from the fitting of specular XRR as a function of temperature are displayed in Fig. 11. The sudden increase in the surface roughness at 120°C can be understood from the point of the formation of hydrogen bonding in different regions of the PHB film. In the PHB film surface, the crystalline and amorphous regions coexist. It is well known that the C=O groups in PHB can form hydrogen bonding with the O—H groups in PVPh. The increase of hydrogen bonds between the C=O group of PHB and O—H group of PVPh during the heating process can be proved by the Grazing reflection-absorption infrared spectroscopy. Figure 12 displays the spectra of the bilayer PHB/PVPh and neat PVPh in the C=O stretching band region. The PVPh film does not show any band in this region. The two strong peaks located at 1744 and 1726 cm^{-1} are assigned to the C=O stretching bands of the amorphous and crystalline phase of PHB, respectively. The peak intensity ratio of 1726 cm^{-1} /1744 cm^{-1} increases with temperature which implies the occurrence of cold crystallization. Moreover the intensity around 1708 cm^{-1} increases obviously when the temperature is above 115°C. As the peak at 1708 cm^{-1} is assigned to the C=O stretching bands hydrogen bonded with the O—H group of PVPh, it can be stated that the hydrogen bonds at the interface of PHB/PVPh increases significantly at 115°C.

As the structure in crystalline phase is much more stable and stiffer than that in amorphous phase, it is expected that the molecular chains of PHB from the amorphous part are relatively easier to interact with the PVPh substrate. The difference of the interaction at the interface of PHB/PVPh may enlarge the height difference between the crystalline and amorphous regions at temperatures above the T_g of PVPh and consequently increase the roughness of the free surface. When the temperature is approaching to the melting point of PHB, the PHB

crystallites melt gradually and the heterogeneous surface induced by the crystallization becomes relatively more homogeneous, resulting in the dissipation of height difference. Hence, the sudden increase in surface roughness at 120°C and the fact that the temporary absence of Kiessig fringe at smaller q_z is presumably caused by hydrogen bonding-induced roughness. Here it should be noted that how powerful the X-ray reflectivity for detecting the subtle change of film surface which is hard to be tracked by other methods. Based on the sensitivity, the specular and off-specular X-ray technology can be further widely applied for characterizing polymer-polymer interface, which plays a very important role in the properties of functional polymer films, such as all-polymer optical devices.

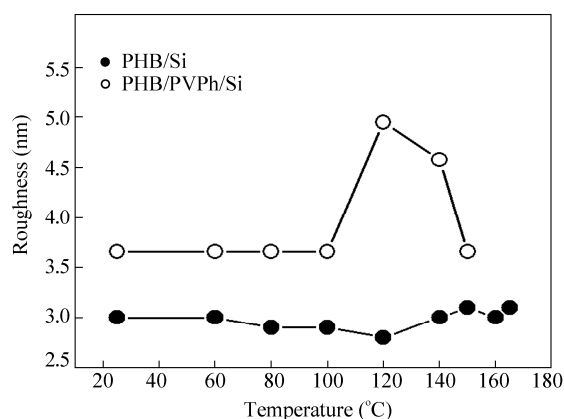


Fig. 11 The change of surface roughness of a single PHB layer and a PHB/PVPh double-layer on Si in the temperature range of 25–170°C

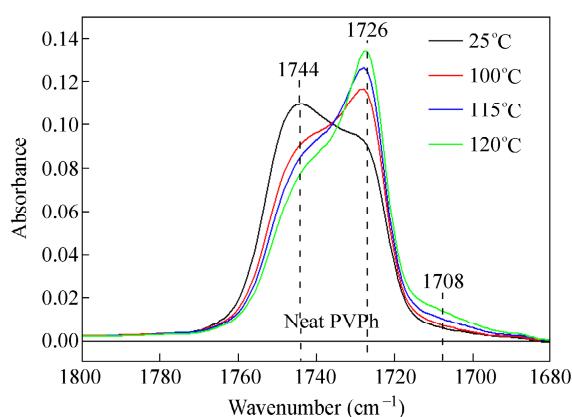


Fig. 12 The spectra of the bilayer PHB/PVPh and neat PVPh in the C=O stretching band region

The Effect of PVPh Substrate on the Recrystallization and Melting Behavior of PHB

When the crystallization and melting behavior of 40.3 nm thick PHB on 22.5 nm thick PVPh is compared with that of 45.6 nm thick PHB on Si, one similarity and several differences can be identified. Both samples exhibit the increment of peak intensity in the heating process. However the absolute (020) peak area of PHB on the PVPh substrate is much smaller than that on the Si wafer. Moreover, in the melting process, the PHB crystals on the PVPh sublayer show a lower melting temperature. Unlike the situation on Si substrate where the melt of crystals begins at 140°C, the melting of PHB on PVPh substrate takes place at 120°C (10% dropping down) followed by a plateau stage (120°C to 140°C), and a 90% peak intensity dropping down is found in the range of 140°C to 160°C.

At room temperature, the crystallization degree of PHB on the PVPh substrate is much lower than that on the Si wafer. The result is unexpected. Room temperature is much lower than the T_g of PVPh, therefore, PVPh sublayer is in its glassy state and can be regarded as a kind of solid substrate. The interaction of hydrogen bonding should not occur at this temperature. Thus the crystallization of PHB should not be depressed. The opposite fact implies that PVPh sublayer is very different from the solid substrate and the interaction of hydrogen bonding forms even in the glassy state of PVPh. The interaction between PVPh and PHB may increase the T_g of PHB to be higher than the room temperature which results in the low crystallization degree at room temperature.

In the recrystallization process, PHB on PVPh substrate also shows the increment of crystallization suggesting some parts of PHB molecular chains in the amorphous phase are not hydrogen bonded to PVPh chains and can pack into lamellae. In the melting process, the PHB crystals on PVPh sublayer feature a three-section melting curve separated by a plateau region of 120–140°C. The crystals melt in the first region should relate to the premelting of the relatively thinner lamellae within the lamellar stacks or surface melting of the crystals. The crystals with the thicker lamellar thickness which form *via* cold crystallization and/or

recrystallization at higher temperatures melt in the third region. By contrast, the crystals of PHB on Si substrate melt continuously. If one assumes that the melting temperature is only related to the lamellar thickness of PHB in this system, it could be inferred that the distribution of PHB lamellar thickness on PVPh sublayer is segmented. The existence of PVPh sublayer changes the distribution of PHB lamellar thickness from a continuous state to a discontinuous one.

CONCLUSIONS

The evolution of surface morphology of single PHB layer and PHB/PVPh double layers deposited on Si substrate during the heating process is successfully monitored by the X-ray diffraction, specular and off-specular XRR. The results indicate that the change of thickness and surface roughness caused by the pre-melting of PHB crystals is relatively small for PHB/Si, whereas the surface roughness and the intensity of Yoneda peak of PHB in the PHB/PVPh/Si system exhibit a non-monotonic change with varying temperature. In this case, the surface roughness of PHB layer reaches its maximum at 120°C. The significant increase in the roughness parameter is presumably induced by the change of intrinsic roughness at the interface between PVPh and PHB. At the interface, the occurrence of interaction contributes to the non-monotonic variation in surface sensitive X-ray diffractions. Concerning with the effect of PVPh sublayer on the crystallization and melting behavior of PHB, the crystallization of PHB thin film is even inhibited on the glassy surface of PVPh sublayer. In the melting process, the PHB crystals on PVPh sublayer feature a three-section melting curve separated by a plateau region of 120–140°C. And the distribution of PHB lamellar thickness on PVPh sublayer may be segmented.

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