



Rheology Behaviours of Miscible Amorphous Poly(3-hydroxybutyrate)/Poly(ethylene oxide)/Poly(*p*-vinylphenol) Blends

Q.Q. JIN^{1,2}, Q. CHEN^{1,2}, K.X. WANG^{1,2}, G.Z. DING^{1,2,*} and J.P. LIU^{1,2,*}

¹College of Chemistry and Materials Science, Huaibei Normal University, Anhui, P.R. China

²Collaborative Innovation Center of Advanced Functional Composites, Anhui, P.R. China

*Corresponding authors: E-mail: dinggz@chnu.edu.cn; jpliu@chnu.edu.cn

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Much attention has been focused on the development and investigation of polymer blends in previous years. The miscibility and rheology behaviours of poly(3-hydroxybutyrate) (PHB), poly(ethylene oxide) (PEO) and poly(*p*-vinylphenol) (PVPh) blends are studied in this work. The linear dynamic viscoelasticity of PHB/PEO/PVPh blends with miscible amorphous composition are investigated by the oscillatory shear measurements. It shows that time-temperature superposition principle (TTS) is applicable for blends. The Han plot ($\log G'$ vs. $\log G''$) is temperature independent, however, the slopes in the terminal region are much less than 2 and become smaller with the addition of poly(ethylene oxide) content. It is considered that this phenomenon might be resulted from the presence of whole hydrogen bonding change (the self-associated interaction and the hydrogen bonding with hydroxyl group, ether group and ester group) in the blends. This conclusion is supported by the Fourier transform infrared spectroscopy analysis.

Keywords: Hydrogen bonding, Miscibility, PHB/PEO/PVPh blends, Rheology behaviours.

INTRODUCTION

Blending polymer is regarded as a convenient route for the development of new polymeric materials application. Generally, the polymer blends can be divided into completely miscible, partially miscible and immiscible systems. Up to now, there are many reports on the development and investigation of polymer blending miscibility. It is suggested that the miscibility of polymer blends be strongly influenced by many factors, such as molecular weight, chemical structure, sample preparation, compositions, crystallization temperature, pressure, *etc.* Especially, the polymer miscibility is determined significantly by the molecular interaction between components. For example, the polymer blend systems with specific hydrogen bonding interaction are interesting and widely investigated by many researchers [1-16]. It is suggested that hydrogen bonding interaction be an important mechanism to expand the range of miscible polymer blends. As is known to all, the miscibility between compositions varies with the solubility parameters. When there are no favourable interactions within compositions and no matching solubility parameters with each other, the mobility of blends is investigated rarely. On the contrary, if favourable hydrogen bonding interaction is present, miscibility can also be found even if the solubility parameter difference between compositions goes up to $3.0 \text{ (cal cm}^{-3}\text{)}^{1/2}$.

At the same time, the rheological properties of polymer blends are also strongly influenced by hydrogen bonding [13,16-21]. For the miscible polymer blends with no specific interaction between compositions, the time-temperature superposition principle (TTS) of oscillatory shear measurements is valid only when there is a small difference in glass transition temperature between components within polymer blends [21]. Then, when the difference of glass transition temperature between components increases, the TTS regulation is in invalidation for the polymer blend, which is resulted from the concentration fluctuations and dynamic heterogeneity within blend [17]. However, the TTS principle is still applied for the polymer blend with the hydrogen bonding interaction between compositions, even if the difference of glass transition temperature between compositions becomes higher or more than 199 °C. For example, the polymer blending systems of poly(*p*-vinylphenol) (PVPh)/poly(vinylacetate) (PVAc), PVPh/poly(vinyl methyl ether) (PVME), PVPh/poly(2-vinylpyridine) (P2VP) and PVPh/poly(4-vinylpyridine) (P4VP) go through a special behaviour due to the existence of hydrogen bonding interaction [16].

Poly(3-hydroxybutyrate) (PHB) has been developed as one of the potential candidates for biodegradable plastics and produced by a wide variety of bacteria [22]. However, poly(3-hydroxybutyrate) is both stiff and brittle due to the presence

of large crystal during the produce process. Therefore, blending of polymer poly(3-hydroxybutyrate) is performed to avoid some material disadvantages. Then, poly(ethylene oxide) (PEO) is chosen to blend with polymer poly(3-hydroxybutyrate) and PHB/PEO polymer blend has been attracted for focusing on due to its biocompatibility and biodegradability [23-26]. Poly(*p*-vinyl phenol) (PVPh) is an amorphous polymer and is a proton donor offering excellent potential for hydrogen-bonding interaction. The miscible blend systems of PHB/PVPh [27-35] and PEO/PVPh [36-40], as a result of forming hydrogen bonding interaction between compositions, have also been investigated by many researchers. Based on the above background, it is important for PHB/PEO/PVPh polymer blend in polymer industries. Therefore, as a typical ternary blend system, it is significant to investigate the property of PHB/PEO/PVPh polymer blend, contributing to not only understand the basic principle of polymer blending further but also direct its industry application of material performance. However, the investigation of PHB/PEO/PVPh polymer blend performance, especially for the rheology property, can be found rarely. In this work, the rheological behaviours of the miscible amorphous PHB/PEO/PVPh blend system are studied by oscillatory shear measurements. The characteristics of TTS and Han plots are discussed for polymer blends in details.

EXPERIMENTAL

Poly(3-hydroxybutyrate) (PHB) with $M_w = 358,000$ (T_g 3 °C, T_c 53 °C, T_m 165 °C), poly(ethylene oxide) (PEO) (T_m 65 °C) with $M_w = 200,000$ and poly(*p*-vinylphenol) (PVPh) (T_g 182 °C) with $M_w = 20,000$ used in this work were purchased from Aldrich.

Blends preparation: The PHB/PEO/PVPh blends were dissolved in a mixed solvent of tetrahydrofuran and chloroform (50/50 v/v) as a 1 % solution according to desired weight ratio. Then the blends were kept at room temperature for 48 h to evaporate solvent. Finally, the blends were dried further under vacuum at 65 °C for 7 days and were kept under the same condition till the experiment is performed.

Detection method: The glass transition temperature (T_g) measurement was performed by differential scanning calorimetry (DSC) (NETZSCH 204 F1). Differential scanning calorimetry curves were recorded by a heating rate of 20 °C/min in the second scan and T_g was taken as the midpoint of glass transition.

Wide angle X-ray diffraction (WAXD) measurements for the polymer blending samples, isothermally crystallized at room temperature from melt, were performed using the X-ray diffractometer (Bruker D8 Advance) and taking advantage of CuK_{α} as X-ray radiation source with a 40 kV working voltage of and 40 mA current.

Rheological measurements were performed on a HAAKE Mars-II rheometer with Modular Advanced Rheometer System. The blending samples with 8 mm diameter and 1 mm thickness were compression-molded ahead of schedule. The oscillatory shear measurements were performed on parallel-plate fixture. The angular frequency was ranged from 0.04 to 100 rad/s in linear viscoelastic zone (1 %) at different temperature (from $T_g + 40$ °C to $T_g + 70$ °C). Storage modulus

G' and loss modulus G'' as a function of angular frequency were obtained at different temperature and the master curves for G' and G'' were gained from the TTS principle at a reference temperature of $T_g + 40$ °C.

Fourier transform infrared spectroscopy was recorded on spectrometer (Nicolet Nexus 470, USA), where 16 scans were collected with a spectral resolution of 4 cm^{-1} . The solution (3 % w/v) containing the polymer blend was cast onto potassium bromide disk at room temperature and then dried under vacuum at 65 °C for 7 days. The sample thickness was moderate so as to obey the Beer-Lambert law.

In addition, the film morphology of blending samples is observed using atomic force microscopy (AFM) (Veeco Nanoscope Multimode 8.0) with tapping mode. The scanning rate is varied from 0.1 to 0.3 Hz. Silicon tip with a resonant frequency of about 300 kHz is selected. To obtain desirable results, different regions of samples are selected to scan under the atmosphere environment and at room temperature.

RESULTS AND DISCUSSION

Differential scanning calorimetry and wide angle X-ray diffraction: Fig. 1 gives DSC thermogram of PHB/PEO/PVPh blends for different compositions. It can be found that only one T_g temperature can be investigated for each polymer blend sample. The single T_g temperature changes along the blend compositions and is intermediate between the T_g of the neat polymers. As is known to all, miscible polymer blends display a single-albeit broad T_g temperature when it is examined by thermal measurement. This result shows that the PHB/PEO/PVPh polymer blends investigated in this paper are all miscible in the amorphous regions.

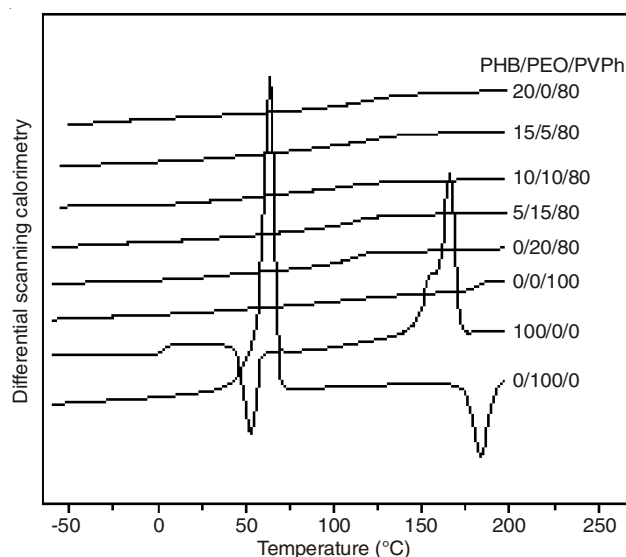


Fig. 1. Differential scanning calorimetry traces of the PHB/PEO/PVPh polymer blends with various compositions by heating at 20 °C/min

Poly(3-hydroxybutyrate) and poly(ethylene oxide), with biocompatibility and biodegradability are crystalline polymers and poly(*p*-vinylphenol) is wholly amorphous polymer. Fig. 2 shows the powder WAXD results of PHB/PEO/PVPh blends with different compositions used in this paper. The crystal peaks of polymer blends cannot be investigated in the WAXD

curves. It indicates that the polymer blends are completely homogeneous amorphous phase, which suggests the addition of poly(*p*-vinylphenol) prevent the crystallization process of poly(3-hydroxybutyrate) and poly(ethylene oxide) in the PHB/PEO/PVPh from blending. The result is consistent with the DSC measurement conclusion. Therefore, the blend indicates an amorphous state when the content of poly(3-hydroxybutyrate) or poly(ethylene oxide) in the blend is reduced by 20 %, as reported in the previous literatures [31,36]. In addition, the rheology behaviour measurement (TTS principle and Han plots) of miscible amorphous system behaves stably without the effect of crystalline and can be drawn to a regular and simple rule conveniently. Therefore, in this work, we chose the homogeneous amorphous compositions to examine the rheological behaviour of PHB/PEO/PVPh blending, aim to emphasize the effect of hydrogen bonding interaction between the PHB/PVPh and PEO/PVPh compositions on the dynamic viscoelasticity. On the contrary, poly(3-hydroxybutyrate) or poly(ethylene oxide) molecules are able to form crystal within the blends when the poly(*p*-vinylphenol) content decreases, thus the physical gelation phenomena resulted from crystallization can be observed for the crystalline/amorphous compositions of blends, which will be discussed in the next paper.

The storage modulus G' and loss modulus G'' are significant property parameters of rheological measurement and refer to the viscoelasticity of polymer blends, but the viscosity is also an important property of the rheological measurement. In this work, we chose time-temperature superposition principle (TTS) and the Han plot ($\log G'$ vs. $\log G''$) to examine the rheological behaviour of PHB/PEO/PVPh blending, aim to emphasize the effect of hydrogen bonding interaction between

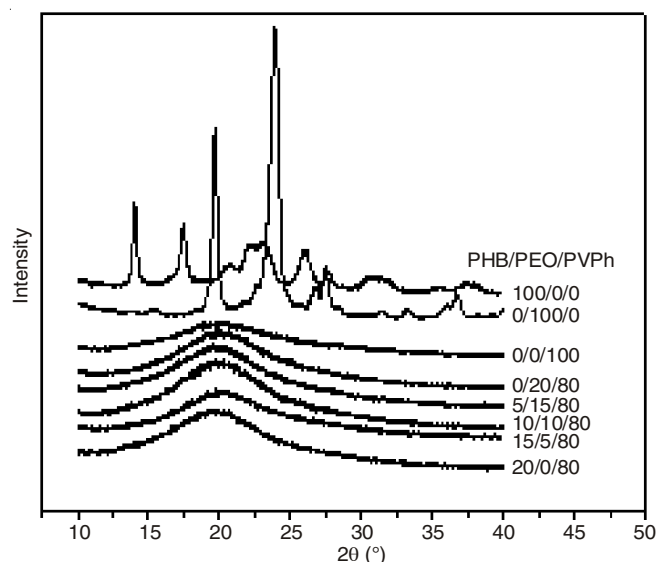


Fig. 2. Wide angle X-ray diffraction patterns for PHB/PEO/PVPh polymer blends with different compositions crystallized isothermally at room temperature

compositions on the dynamic viscoelasticity. It can be drawn a conclusion here by the current modulus measurements and analysis and the relation between the viscosity and physical gelation of PHB/PEO/PVPh blend caused by the crystallization effect will be discussed in the next paper and as a continuous work of this paper.

Linear dynamic viscoelasticity of the PHB/PEO/PVPh blends: The dynamic frequency scanning has been investigated for the PHB/PEO/PVPh blends, as shown in Fig. 3.

The master curves of PHB/PEO/PVPh blends with different compositions have been shown clearly from $T_g + 40$ °C to T_g

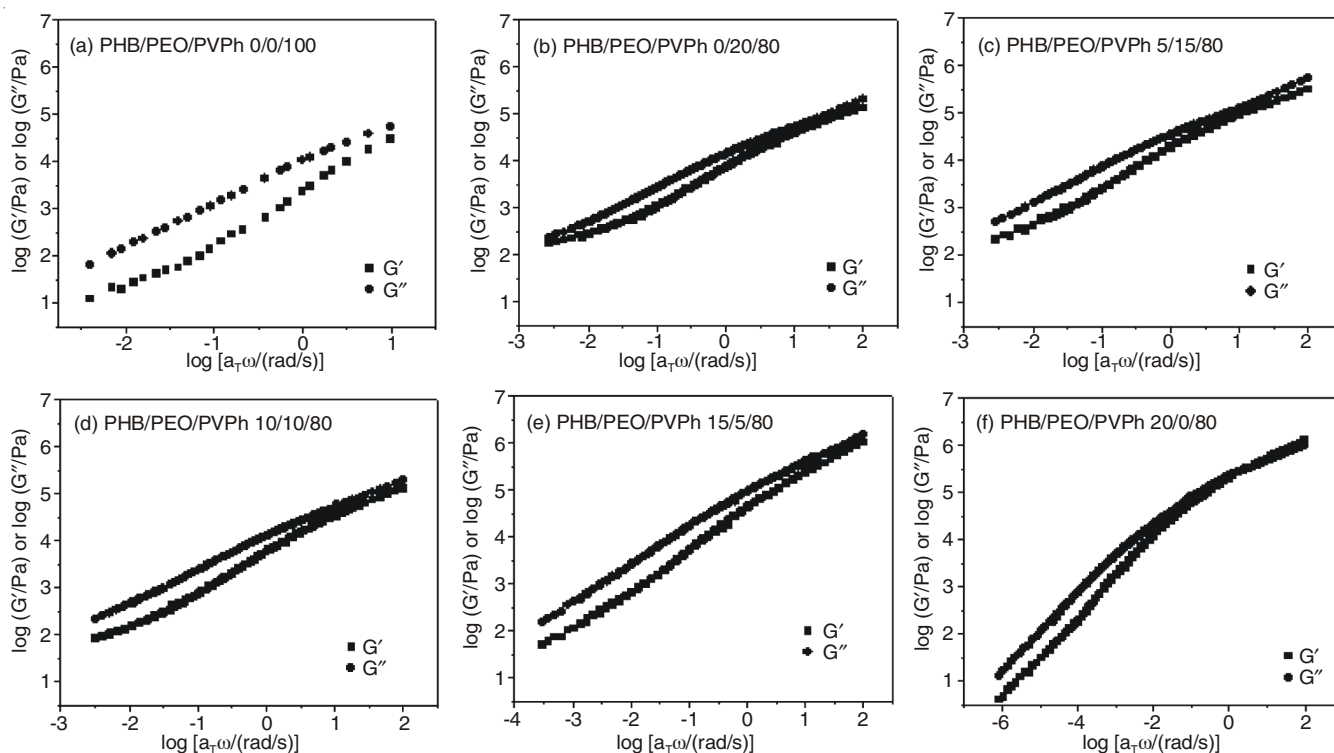


Fig. 3. Master curves of PHB/PEO/PVPh polymer blends for different compositions system: (a) 0/0/100, (b) 0/20/80, (c) 5/15/80, (d) 10/10/80, (e) 15/5/80 and (f) 20/0/80, reference temperature is $T_g + 40$ °C

+ 70 °C. The horizontal shift factor (a_T) is calculated using a time-temperature superposition software of HAAKE company with the WLF expression [41]:

$$\log a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \quad (1)$$

where the a_T is the horizontal shift factor, T and T_r are the experiment temperature and reference temperature ($T_g + 40$ °C), respectively. C_1 and C_2 are the constant. It can be investigated that the master curves show temperature independence for all polymer blending systems. This phenomenon indicates that the TTS principle is in validation for our examined polymer blends under the temperature zone from $T_g + 40$ °C to $T_g + 70$ °C. Therefore, this result further indicates that the PHB/PEO/PVPh blends are miscible here. At the same time, it implies that concentration fluctuations and dynamic heterogeneity are not present in the PHB/PEO/PVPh polymer blends.

The Han plots of PHB/PEO/PVPh polymer blends are also investigated and the results are shown in Fig. 4 for different blend compositions. The Han plot ($\log G'$ vs. $\log G''$) was put forward to examine the order-disorder transition of block copolymer [42,43] and subsequently Han plots were also used to measure the miscibility of polymer blends [16,19]. It was proved that for a miscible polymer blend, the Han plots were independent of temperature and the slope of Han plots in the terminal zone were also close to 2 simultaneously. It can be investigated that the Han plot ($\log G'$ vs. $\log G''$), as shown in Fig. 4, is independent of investigated temperature for all the polymer blends. However, the curvatures of Han plots in the terminal region are much less than 2 evidently. In addition, we have also investigated the curvature change trend of Han plots in the terminal region (Fig. 5). It indicates that the

curvatures become much larger as increasing the poly(3-hydroxybutyrate) content or decreasing the poly-(ethylene oxide) content within the blends in this work and the slope of pure poly(*p*-vinylphenol) polymer in the terminal region is intervenient between the 10/10/80 (PHB/PEO/PVPh) and 5/15/80 blends. A conclusion has been drawn that the PHB/PEO/PVPh blends are immiscible in this work seemingly. However, the DSC and WAXD results indicate that the PHB/PEO/PVPh blends prepared in this work are miscible in the amorphous polymer blend systems. In addition, the dynamic frequency scanning investigation also supports that the polymer blends here are all miscible and the concentration fluctuation and dynamic heterogeneity cannot be found yet in the polymer blends from TTS principle results. It looks like contradictory from the above results apparently. As a matter of fact, it can be considered that the PHB/PEO/PVPh blends are miscible indeed and the abnormal phenomenon of Han plot curvature may come from the presence of hydrogen bonding interaction within the blend compositions [16]. In order to confirm the hydrogen bonding interaction between components, we also carried out the FTIR spectra measurement.

Fig. 6 shows the FTIR spectra of poly(3-hydroxybutyrate), poly(ethylene oxide), poly(*p*-vinylphenol) and its blends for the 3800-3000 cm^{-1} hydroxyl stretching region. In the hydroxyl stretching region, the pure poly(*p*-vinylphenol) polymer has two absorption bands for the overall OH stretching band owing to the free hydroxyl group (about 3520 cm^{-1}) and the self-associated (about 3330 cm^{-1}) hydroxyl group between hydroxyl and hydroxyl group of poly(*p*-vinylphenol). The pure poly(3-hydroxybutyrate) and poly(ethylene oxide) display no absorption bands. However, the polymer blends have different absorption because of the hydrogen bonding interaction change.

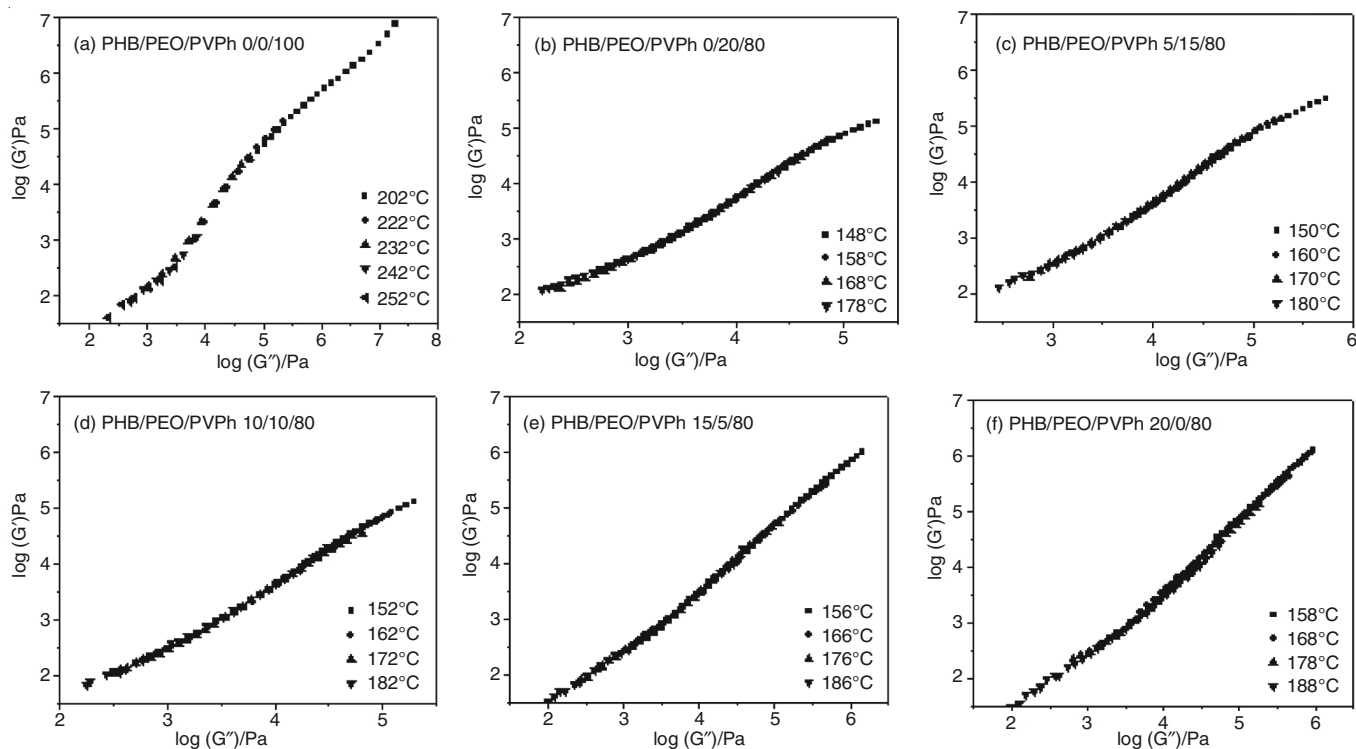


Fig. 4. Han plots of PHB/PEO/PVPh blends for different compositions: (a) 0/0/100, (b) 0/20/80, (c) 5/15/80, (d) 10/10/80, (e) 15/5/80 and (f) 20/0/80

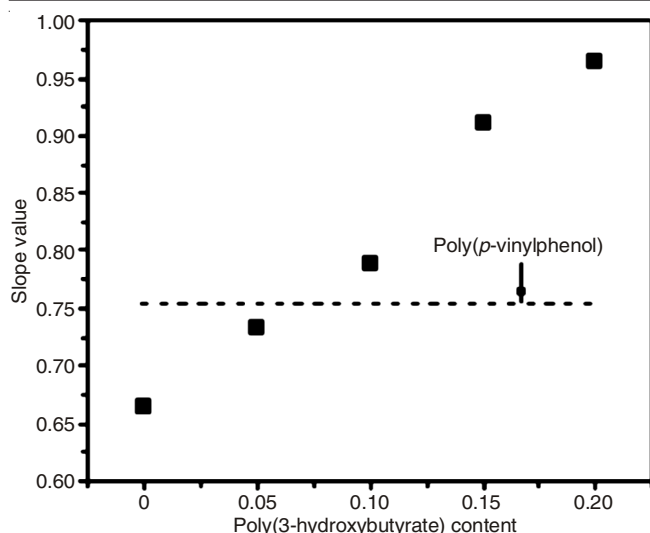


Fig. 5. Curvature values of Han plots in terminal region vs. poly(3-hydroxybutyrate) content of PHB/PEO/PVPh blends

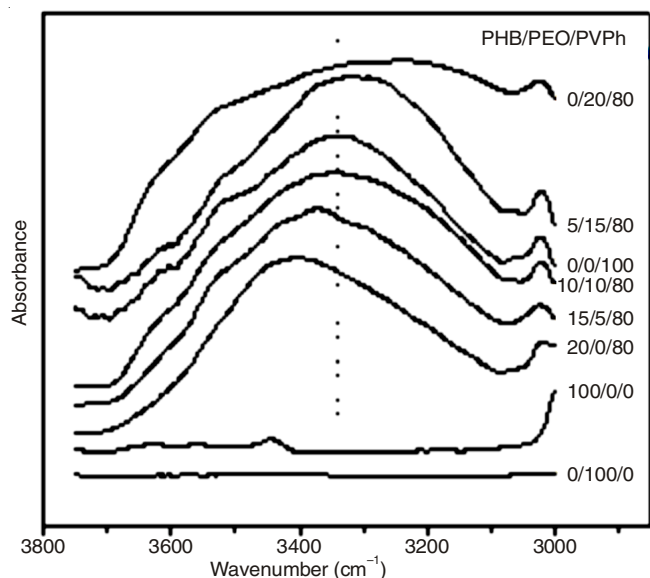


Fig. 6. FTIR spectra of poly(3-hydroxybutyrate), poly(ethylene oxide), poly(*p*-vinylphenol) and polymer blends within 3800-3000 cm^{-1} hydroxyl stretching region

Compared with the pure poly(*p*-vinylphenol), the intensity of free hydroxyl group of blends decreases and its absorption band of the 0/20/80 (PHB/PEO/PVPh) blends is shifted to the lower wavenumber while the absorption band of the 20/0/80 (PHB/PEO/PVPh) blends is shifted to the higher wavenumber. The absorption band of PHB/PEO/PVPh blends is shifted to the much higher wavenumber with the poly(3-hydroxybutyrate) content increase within polymer blends. They are consistent with the result of the literatures [30,44].

As is known to all, the relative strength of self-associated (about 3330 cm^{-1}) hydroxyl groups within poly(*p*-vinylphenol) is much stronger than the hydrogen bonding interaction between hydroxyl group in poly(*p*-vinylphenol) and ester group in poly(3-hydroxybutyrate), however, the relative interaction of self-associated hydroxyl groups in poly(*p*-vinylphenol) is weaker than the hydrogen bonding interaction between hydroxyl group in poly(*p*-vinylphenol) and ether group within polymer poly(ethylene oxide) [45]. Therefore,

the intensities of whole hydrogen bonding (self-associated and the hydrogen bonding) within 0/20/80 (PHB/PEO/PVPh) blends are greater than those of the 20/0/80 blends and spontaneously the intensities of whole hydrogen bonding of PHB/PEO/PVPh blends become weakened with the addition of poly(3-hydroxybutyrate) component content. In all, the hydrogen bonding interaction (self-associated and hydrogen bonding) can be found certainly for the pure poly(*p*-vinylphenol) and the polymer blends. As a result, the slope of Han plots in the terminal region, much less than 2, can be induced by the hydrogen bonding interaction for pure poly(*p*-vinylphenol) and the blends. Finally, the slope of Han plots in the terminal region of 0/20/80 blend is much less than the 20/0/80 blends obviously and the slopes of Han plots of the blends become more larger with the addition of poly(3-hydroxybutyrate) content (Fig. 5) and simultaneously the slope of pure poly(*p*-vinylphenol) in the terminal region is intervenient between the 10/10/80 and 5/15/80 blends.

It is noted that that the thin film morphology of blending samples discussed above are also investigated, as shown in Fig. 7. It indicates that the uniform surface morphology is present within all samples, which may be the reason that PHB/PEO/PVPh polymer blends are all miscible in the amorphous regions. However, the surface roughness of sample morphology is enhanced with the addition of poly(3-hydroxybutyrate) component content within blends and the roughness of pure poly(*p*-vinylphenol) in the surface morphology is indicated between the 10/10/80 and 5/15/80 blends. The formation of this morphology may be mainly resulted from the results that the intensities of whole hydrogen bonding of PHB/PEO/PVPh blends become weakened with the addition of poly(3-hydroxybutyrate) component content and simultaneously the whole hydrogen bonding interaction of pure poly(*p*-vinylphenol) is intervenient between the 10/10/80 and 5/15/80 blends. It is known that the material property is mainly affected by the polymer surface morphology. Therefore, it can be gained that the miscibility of blending and sample morphology is mainly dependent on the whole hydrogen bonding interaction within polymers and the slope of Han plots in the terminal region can be induced by the hydrogen bonding interaction for pure poly(*p*-vinylphenol) and the blends.

In addition, the classical linear dynamic viscoelasticity behaviours are performed as following equations [41]:

$$\log G' = 2 \log \omega + \log (J_e^0 \eta_0^2) \quad (2)$$

$$\log G'' = \log \omega + \log \eta_0 \quad (3)$$

$$\log G' = 2 \log G'' + \log J_e^0 \quad (4)$$

where G' , G'' , ω , J_e^0 and η_0 is storage modulus, loss modulus, angular frequency, steady-state shear compliance and zero steady-state shear viscosity, respectively. On the above rheology discussion, it can be found that G' and G'' of all samples behave the similar change trend with the angular frequency, that is the modulus increases with the addition of angular frequency, as the above classical viscoelasticity regulation. However, the curvatures of the master curves and Han plots in the terminal zone (the angular frequency is very small) deviate from the classical linear dynamic viscoelasticity obviously. The transition in the terminal zone was usually used to study the change of

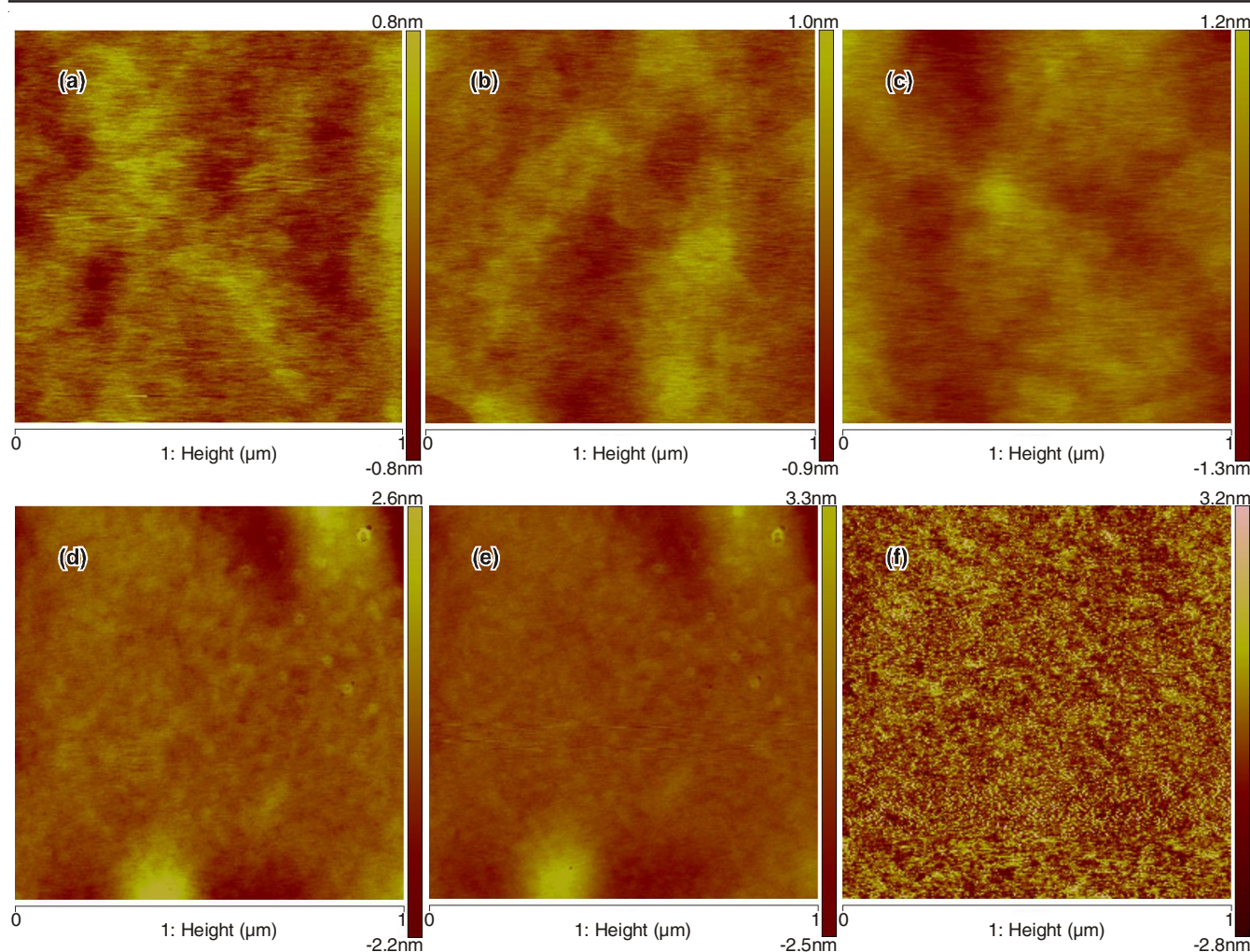


Fig. 7. Atomic force microscopy height images of PHB/PEO/PVPh blends for different compositions: (a) 0/20/80, (b) 5/15/80, (c) 0/0/100, (d) 10/10/80, (e) 15/5/80 and (f) 20/0/80

polymer viscoelasticity and was investigated to indicate the microcosmic transition within polymer molecules. It shows that the abnormal phenomenon of curvatures mainly comes from the presence of hydrogen bonding interaction within the blend compositions. Furthermore, the change degree of curvatures in the terminal zone is mainly dependent on the intensity of hydrogen bonding interaction within polymer blends.

Conclusion

In all, the hydrogen bonding interaction is present in the PHB/PEO/PVPh blends for sure. The presence of hydrogen bonding interaction within PHB/PEO/PVPh blends has a direct effect on the miscibility, crystallization and dynamic viscoelasticity. The DSC and WAXD results indicate that the addition of poly(*p*-vinylphenol) prevents the crystallization of poly(3-hydroxybutyrate) and poly(ethylene oxide) in the PHB/PEO/PVPh blends due to the presence of hydrogen bonding. According to the linear dynamic viscoelasticity investigation of miscible PHB/PEO/PVPh blends, the TTS principle is valid within examined temperature zone. Therefore, we can infer that the investigated PHB/PEO/PVPh blends are miscible and there are no concentration fluctuations and dynamic hetero-

geneity within the blends. However, for the abnormal phenomenon of Han plot, the slopes in the terminal zone are much less than 2 obviously and become smaller with increasing of the poly(ethylene oxide) content. It is suggested this phenomena is due to the presence of hydrogen bonding interaction alteration within the polymer blends. The intensities of whole hydrogen bonding (self-associated and hydrogen bonding) of 20/80 (PEO/PVPh) blends are greater than the ones of 20/80 (PHB/PVPh) blends and the intensities of whole hydrogen bonding of polymer blends are weakened with the poly(3-hydroxybutyrate) component content addition, according to the FTIR analysis. Therefore, it can be found that the dynamic viscoelasticity of polymer blend are mainly determined by the hydrogen bonding interaction.

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