Miscibility and Rheology Behaviors of Poly(3-hydroxybutyrate)/Poly(p-vinylphenol) Blends with Homogeneous Amorphous Compositions

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ABSTRACT: The miscibility and rheology behaviors of poly(3-hydroxybutyrate) (PHB) and Poly(p-vinylphenol) (PVPh) blends were studied in this work. It was evidenced that the miscible amorphous system of the PHB/PVPh blends was formed when the PHB content was less than 40%(wt). Linear dynamic viscoelasticity of the blends in the amorphous condition was studied through oscillatory shear measurements. Time-temperature superposition principle (TTS) was applicable in the experimental window. The Han plots (log G' versus log G'') were temperature independent, but the curvatures in the terminal region were much less than 2 and became smaller with increasing of the PVPh. It was considered that this phenomenon might come from the presence of the change of the whole hydrogen bonding (self-associated and the hydrogen bonding between hydroxyl group and ester group) in the blends. The Fourier transform infrared spectroscopy analysis supported this conclusion. It was found that the rubber plateau modulus for this blend system did not follow Wu's and Tsenoglou's model. This result was also caused by the presence of the hydrogen bonding. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 617–623, 2011

Key words: miscibility; time-temperature superposition principle; Han plot; rubber plateau modulus; PHB/PVPh; hydrogen bonding

INTRODUCTION

A convenient route for the development of new polymeric materials is to blend polymers. During the last decades much attention has been focused on the development and investigation of binary polymer blends. Generally, the polymer blends can be divided into completely miscible, immiscible and partially miscible systems. Up to now, there are many reports on the miscibility of polymer blends. If the blend is homogeneous, i.e., the components are miscible at the molecular level, the properties are showing a continuous change with the concentration. Otherwise, if the blend is heterogeneous the properties of the pure components are unchanged and preserved in the blend. It was found that the miscibility of polymer blends was strongly affected by many factors, which affected the molecular interaction between two components, such as molecular weight, chemical structure, sample preparation, compositions, crystallization temperature and pressure and so on. Nevertheless, the polymer blend systems with specific interaction, for example, hydrogen bonding, are widely interesting for many researchers.[1–20] It is suggested that hydrogen bonding be an important mechanism to expand the range of miscible polymer pairs since if no favorable interactions are present the miscibility is very rare and is only found when miscibility parameters match each other, if favorable weak interactions are present, miscibility can be found even if the difference in solubility parameters goes up to 0.5 (cal cm^{-3})$^{1/2}$, but when hydrogen bonds are established, it can go up to 3.0(cal cm^{-3})$^{1/2}$.

On the other hand, the rheological properties of miscible polymer blends are strongly influenced by hydrogen bonding.[13,20–25] It is found that, for some miscible polymer blends with no specific interactions between two components, when the difference in glass transition temperature between two components of the blends is small (about 25°C) time-temperature superposition (TTS) principle is in effect.[25] While the difference is larger the TTS is in invalidation which may be affected by concentration fluctuations and dynamic heterogeneity.[21] However, the rheological properties of miscible polymer blends with forming hydrogen bonding are more different. Han group has investigated the linear dynamic viscoelasticity of miscible polymer blends of PVPh/poly(vinylacetate) (PVAc), PVPh/poly(vinyl methyl ether) (PVME), PVPh/poly-(2-vinylpyridine)(P2VP) and PVPh/poly(4-vinylpyridine) (P4VP). It is suggested that, although the
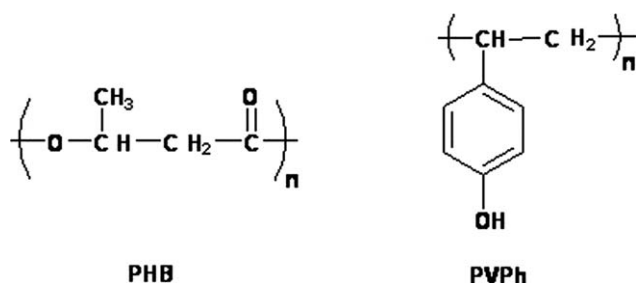
Figure 1 Chemical structures of Poly(3-hydroxybutyrate) (PHB) and Poly(p-vinylphenol) (PVPh).

largest difference in glass transition temperature between two components for four blends is 199°C, the TTS principle is still applied.[20]

The miscible blend of PHB with PVPh, a polymer blend with forming hydrogen bonds according to the chemical structures shown in Figure 1, has been studied by many researchers,[26–36] however, the literature about the rheology of PHB/PVPh blends cannot be seen clearly. In present work, the miscibility and rheological behaviors of this system were studied. The characteristics of time-temperature superposition principle (TTS), Han plots and rubber plateau modulus of the blends were discussed in details.

EXPERIMENTAL

Materials and specimen preparation

Poly(3-hydroxybutyrate) (PHB) with $M_w = 358,000$ and $M_w/M_n = 1.24$ and Poly(p-vinylphenol) (PVPh) with $M_w = 20,000$ and $M_w/M_n = 1.16$ used in this work were purchased from Aldrich.

The PHB/PVPh blends in the desired weight ratio were dissolved in a mixed solvent of tetrahydrofuran and chloroform (50/50 wt) as a 1 wt % solution. Then the blends were kept at room temperature for 48 h for the evaporation of solvent. Next the blends were dried under vacuum at 65°C for seven days and annealed at 160°C in a vacuum oven.

Instruments and experiments

Differential Scanning Calorimetry (DSC) (NETZSCH 204 F1) was used to determine the glass transition temperature (T_g). DSC curves were recorded by a heating rate of 20°C/min in the second scan, and T_g was taken as the midpoint of the transition.

WAXD experiments for the thin film samples were carried out by X-ray diffractometer (BRUKER D8 ADVANCE) using Cu Kα as X-ray radiation source with a voltage of 40kV and a current of 40 mA. Before this measurement the blend samples were stored at room temperature for about 15 days.

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 (5%w/v) containing the blend was cast onto potassium bromide disk at room temperature and then dried under vacuum at 65°C for seven days and annealed at 160°C in a vacuum oven. The thickness of a film was adjusted so that the Beer-Lambert law was obeyed.

Rheological measurements were carried out on a HAAKE Mars-II rheometer with Modular Advanced Rheometer System. The oscillatory experiments of the samples with 8.0 mm diameter and 1.0 mm thickness which were compression-molded ahead of schedule were performed on parallel-plate fixture. The angular frequency was ranged from 0.04 to 100rad/s in linear viscoelastic zone (1%) at different temperatures ($T_g + 30$°C to $T_g + 70$°C). Storage modulus G' and loss modulus G'' as a function of angular frequency were obtained at different temperatures and the master curves for G' and G'' were gained from the time-temperature superposition principle at a reference temperature $T_g + 30$°C.

RESULTS AND DISCUSSION

Miscibility and crystallization determined by DSC and WAXD

Miscible polymer blends display a single-albeit broad-glass transition temperature (T_g) when examined by thermal methods. Figure 2(a) gives differential scanning calorimetry thermograms of PHB/PVPh blends with different compositions. It can be seen that only one T_g can be investigated for each composition. The single T_g changes with compositions, which is intermediate between the T_gs of two neat polymers, as shown in Figure 2(b). This result indicates that the PHB/PVPh blends prepared in this work are miscible in the amorphous regions.

PHB is a crystalline polymer and PVPh is wholly amorphous. If PHB in PHB/PVPh blend is crystallized, the phase separation will occur between the crystal and amorphous regions. The phase separation caused by crystallization will affect on rheological behaviors of the blends. Figure 3 shows the powder WAXD results of PHB/PVPh blends with different compositions. It is clear that, when PHB content is more than 60%, the PHB can crystallize in the blends, the crystallinity of the PHB increases with increasing of PHB contents. When PHB content is less than 40%, the systems are completely homogeneous amorphous phase, which suggests the addition of PVPh prevents the crystallization of PHB in the PHB/PVPh blends. In this work, the rheological behaviors of the homogeneous amorphous compositions of PHB/PVPh blends were studied in details. The rheology property of the physical gelation phenomena caused by the PHB crystallization at higher
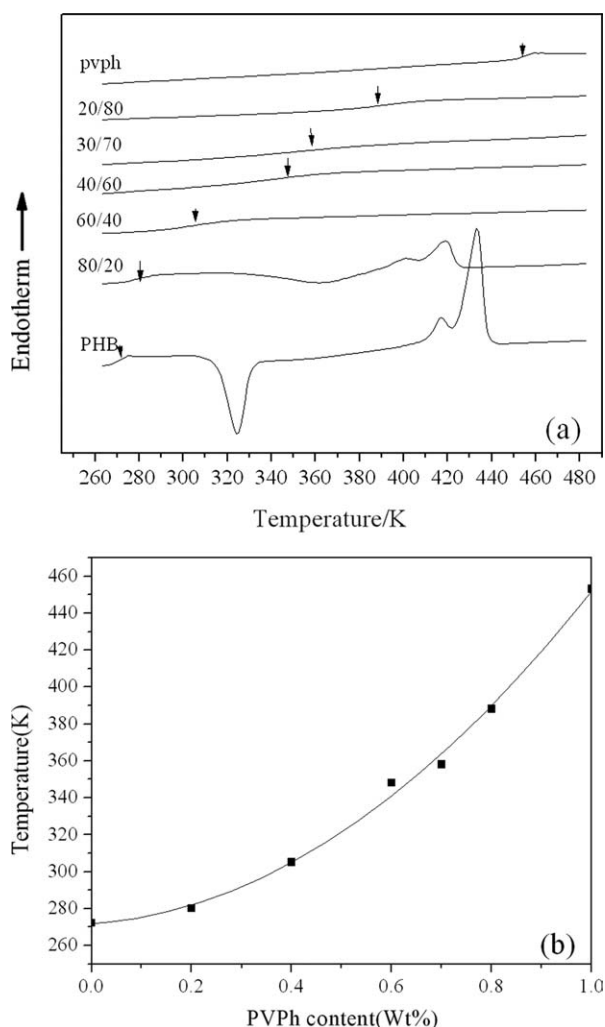
Figure 2 (a) DSC traces of the quenched PHB/PVPh blends recorded during heating at 20°C/min with various compositions. (b) Plot of glass transition temperature (T_g) versus PVPh content of PHB/PVPh blends.

PHB content (more than 40%) will be discussed in next work.

Linear dynamic viscoelasticity of the PHB/PVPh blends

Master curves of the PHB/PVPh blends gained from the time-temperature superposition principle (TTS) were carried out from $T_g + 30$°C to $T_g + 70$°C. The horizontal shift factor (a_T) was calculated using a time-temperature superposition software of HAAKE Company with the WLF expression[37]:

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

Where the a_T is the horizontal shift factor, T and T_r are the experiment temperature and the reference temperature respectively, and the C_1 and C_2 are the

constants. It can be found that the master curves, as shown in Figure 4(a–c), for this blend system show temperature independence, which indicates that the time-temperature superposition principle (TTS) is applicable in the experimental window. This result further proves that the PHB/PVPh blends are miscible, and there are not concentration fluctuations and dynamic heterogeneity for the PHB/PVPh blends. Additionally, as shown in Figure 4(d), the horizontal shift factor (a_T) decreases with increasing of temperatures and shows temperature dependence, indicating the isofree volume conditions are not observed. This may come from the large difference in properties between PHB and PVPh.[13]

Han etc. put forward the Han plot (log G' versus log G'') to research the order–disorder transition of the block copolymer,[38,39] and subsequently Han plots were also employed to study the miscibility of the polymer blends.[20,23] It is believed that, if a polymer blend is miscible, the Han plots are independent of temperature and the curvature of Han plots in the terminal zone are close to 2 simultaneously. In this work, Han plots of PHB/PVPh blends are shown in Figure 5(a–d) for different blend compositions. It can be seen that the Han plot (log G' versus log G'') is temperature independent within the experimental compositions. However, the curvatures of the plots in the terminal region are much less than 2 obviously. At the same time the curvatures of the plots in the terminal region become smaller with increasing of the PVPh content. Normally, the change of the curvature results from concentration fluctuation and dynamic heterogeneity. It seems that the PHB/PVPh blends are immiscible from the result of the
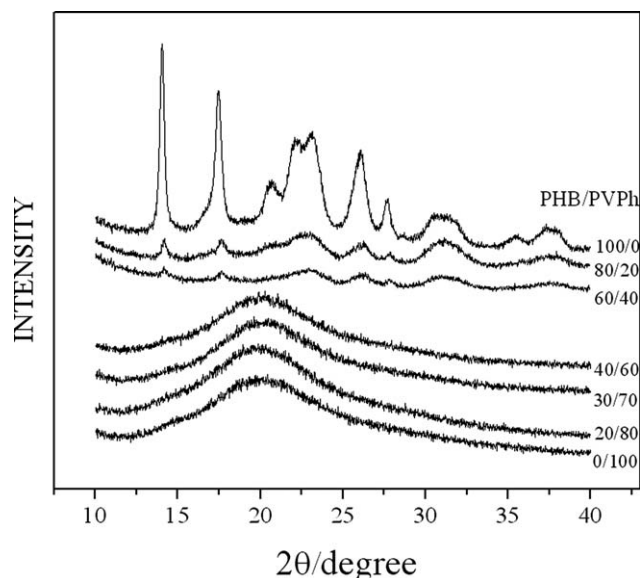
Figure 3 WAXD patterns for PHB/PVPh blends crystallized isothermally at room temperature.
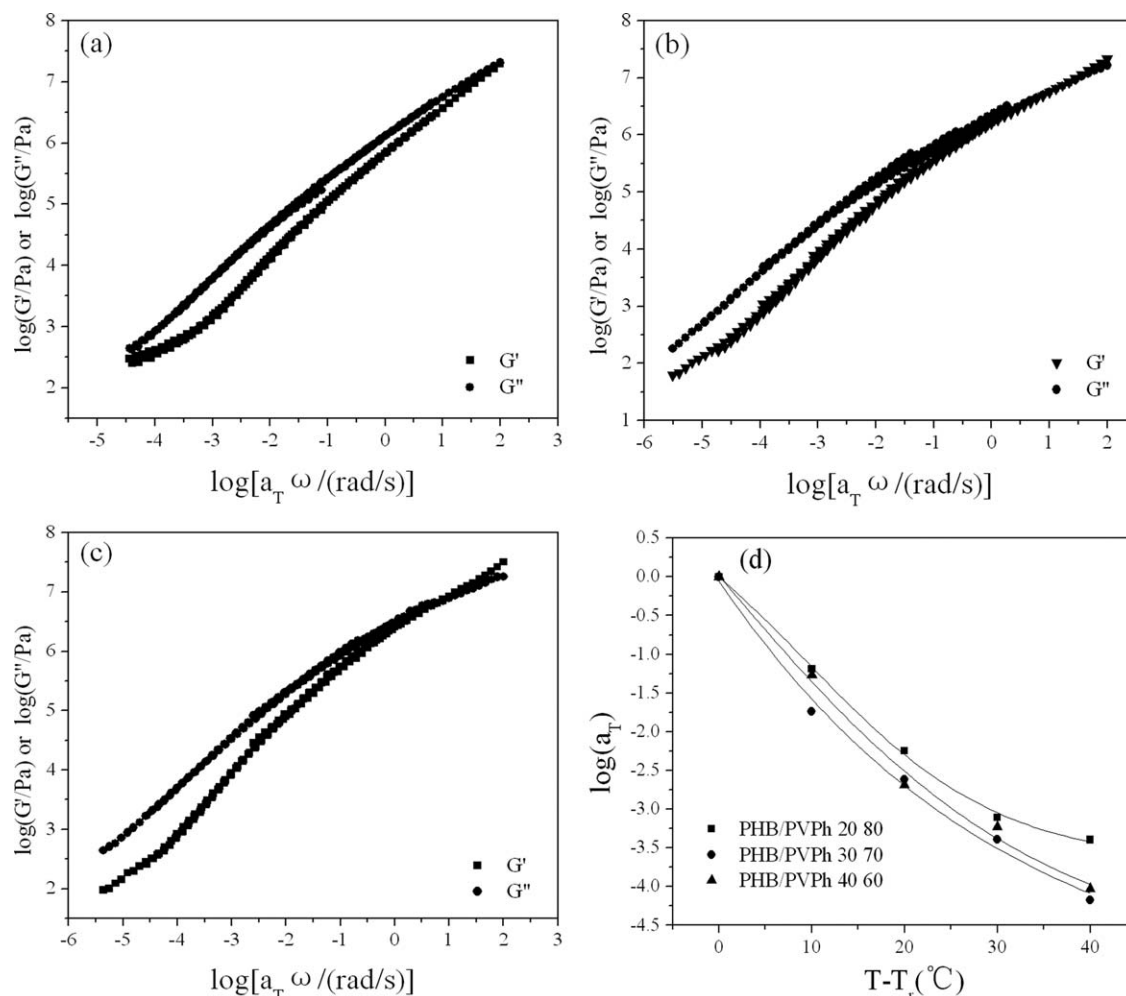
Figure 4 The master curves of PHB/PVPh blends with different compositions of (a) 20/80, (b) 30/70, and (c) 40/60 with a reference temperature of $T_g + 30°C$. (d) Plots of a_T versus T-Tr for PHB/PVPh blends.

Han plots. However, according to above discussion, the time-temperature superposition principle is applicable, which means the PHB/PVPh blends are miscible and the concentration fluctuation and dynamic heterogeneity can be excluded, and the DSC result also indicates that the PHB/PVPh blends prepared in this work are miscible in the amorphous regions. As a matter of fact, it can be considered that the PHB/PVPh blends are miscible and the phenomenon from Han plot may come from the presence of the hydrogen bonding in the blends.[20]

Figure 6 shows the FTIR spectra of PHB, PVPh and its blends recorded at room temperature in the 3800–3000 cm^{-1} hydroxyl stretching region and 1780–1690 cm^{-1} carbonyl stretching region. In the hydroxyl stretching region PVPh shows two absorption bands to the overall OH stretching band owing to the free hydroxyl group (about 3520 cm^{-1}) and the self-associated (about 3310 cm^{-1}) hydroxyl group between hydroxyl and hydroxyl group of PVPh. But the blends behave different contributions with the presence of the hydrogen bonding between hydroxyl

group in PVPh and ester group in PHB. Then the intensity of free and self-associated hydroxyl group decrease with addition of PHB content, and the contribution of the hydrogen bonding hydroxyl group is strengthening and its absorption band is shifted to the higher wavenumber. In the carbonyl stretching region the blends take on two absorption bands of nonassociated (about 1740 cm^{-1}) and hydrogen bonding (about 1716 cm^{-1}) carbonyl group, and there is not crystalline (about 1724 cm^{-1}) carbonyl group like the absorption band of the pure PHB, which is in accord with the results of WAXD. They are consistent with the results of the literature.[30,31]

According to Zhang et al.,[40] the relative strength of self-associated (about 3310 cm^{-1}) hydroxyl groups in PVPh is stronger than the hydrogen bonding between hydroxyl group in PVPh and ester group in PHB. So it can be seen that the intensities of the whole hydrogen bonding (self-associated) of pure PVPh are greater than the ones of the whole hydrogen bonding (self-associated and the hydrogen bonding between hydroxyl group and ester group) of the
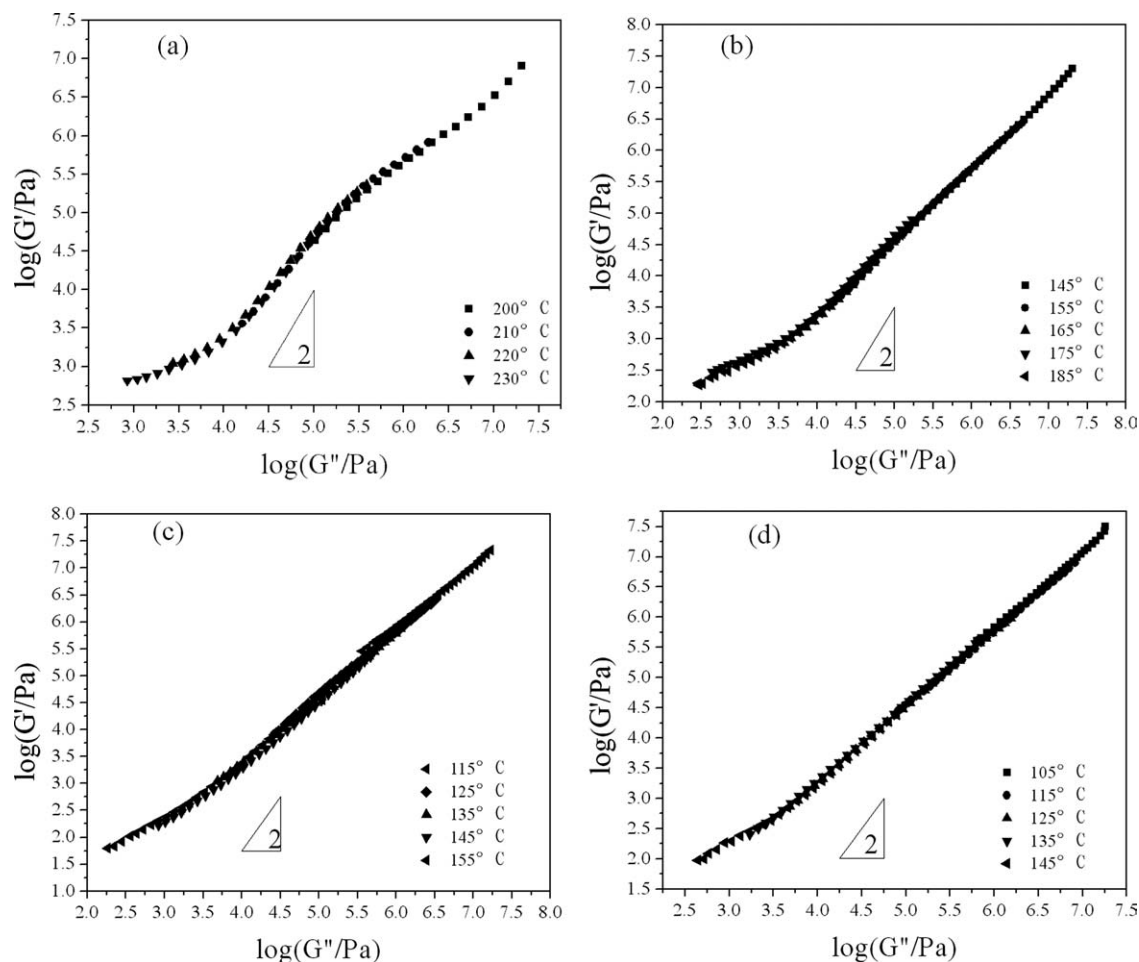
Figure 5 Plots of log G' versus log G'' at different temperatures of PHB/PVPh blends with different compositions of (a) pure PVPh, (b) 20/80, (c) 30/70, and (d) 40/60.

blends and the intensities of the whole hydrogen bonding of the PHB/PVPh blends are enhanced with the component of PVPh from 60 to 80 wt %, which arise from the result that the contribution of the hydrogen bonding between hydroxyl group in PVPh and ester group in PHB is strengthening and its absorption band is shifted to the higher wavenumber with addition of PHB content. It is suggested that the hydrogen bonding (self-associated and the hydrogen bonding between hydroxyl group and ester group) are presented in the PVPh and the blends investigated in this work for sure, and this can induce that the curvatures of the Han plots in the terminal region of pure PVPh and the blends are much less than 2. As a result, it can be attained that the curvature of the Han plots in the terminal region of pure PVPh is much less than the PHB/PVPh blends obviously and the curvatures of the Han plots in the terminal region of the blends become smaller with increasing of the PVPh content. According to the FTIR results [Fig. 6(a)], it can be concluded that the stronger the whole hydrogen bonding is, the smaller the curvatures of the Han plots in the terminal region is. So this result

supports that the singularities of the curvature of the Han plots in the terminal region for the PHB/PVPh blends should come from the presence of the change of the whole hydrogen bonding (self-associated and the hydrogen bonding between hydroxyl group and ester group) in the blends.

Rubber plateau modulus (G_N^0)

Rubber plateau modulus (G_N^0) is a important parameter of rheology.[41–44] Generally, G_N^0 can be calculated from the following semiempirical equation[13,41] using the crossover modulus (G_c) of the dynamic rheological data in the linear viscoelastic region:

$$\log(G_N^0/G_C) = 0.380 + \frac{2.63(\log P)}{1 + 2.45(\log P)} \quad (2)$$

Where P is the polydispersity, and the crossover modulus $G_c = G'(\omega_c) = G''(\omega_c)$. For the PHB/PVPh blends system, the polydispersity of pure PVPh is selected as the polydispersity of the blends. Figure 7 shows the plot of G_N^0 versus PVPh weight fraction
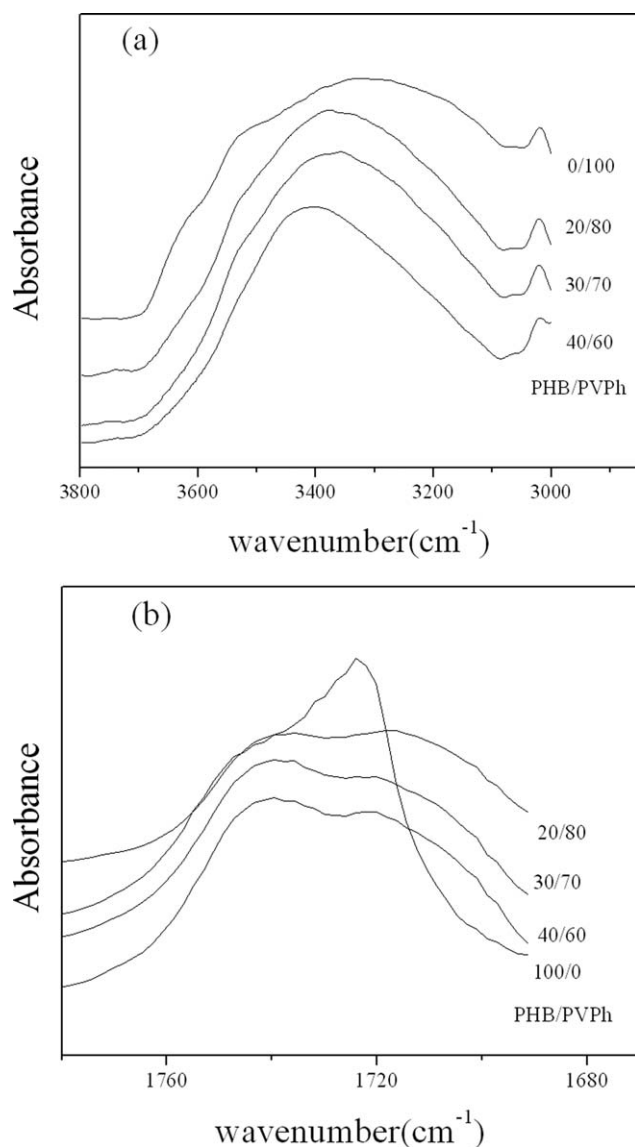
Figure 6 The FTIR spectra of PHB, PVPh and the blends recorded at room temperature: (a) 3800–3000 cm^{-1} hydroxyl stretching region; (b) 1780–1690 cm^{-1} carbonyl stretching region.

for the PHB/PVPh blends system. It is suggested from the experiment data that the rubber plateau modulus (G_N^0) of the PHB/PVPh blends increase with the content of the PVPh from 60 to 80 wt %. This result may come from the difference of the rubber plateau modulus (G_N^0) between the pure PHB and PVPh (G_N^0, PVPh > G_N^0, PHB).

On the other hand, for miscible polymer blend systems with no interchain specific interactions, G_N^0 can be calculated theoretically by Wu's model[44] as following equation:

$$G_N^0 = \phi_1 G_{N1}^0 + \phi_2 G_{N2}^0 \qquad (3)$$

Where G_N^0, G_{Nj}^0 ($j = 1,2$) are rubber plateau modulus of the blend and pure components in the blends

respectively. $\phi_j(j = 1,2)$ is the volume fraction. In addition, Tsenoglou proposed the rubber plateau modulus (G_N^0) formula of the miscible blends in the athermal condition[42]:

$$(G_N^0)^{1/2} = \phi_1 (G_{N1}^0)^{1/2} + \phi_2 (G_{N2}^0)^{1/2} \qquad (4)$$

From Figure 7 it can be seen that the experimental rubber plateau modulus (G_N^0) are much less than that estimated theoretically by Wu's and Tsenoglou's models, which suggests this PHB/PVPh miscible blend systems with hydrogen bonding interaction do not follow the athermal situation. This is mainly attributed to the presence of the contribution of the hydrogen bonding between hydroxyl group in PVPh and ester group in PHB, and Wu's and Tsenoglou's models do not take this into account.[13] The presence of the hydrogen bonding between PHB and PVPh may confine the movement between the chain segments, reduce interchains convolution and block the entanglement between chains of the blends, which, in turn, decreases the rubber plateau modulus of the blends. Additionally, the crossover modulus (G_c) of the pure PVPh in this work, as shown in Figure 5(a), is much larger than the paper reported by Brisson et al.,[13] which may come from the difference of the molecular weight of PVPh and finally affect the rubber plateau modulus (G_N^0) of the PVPh and the blends.[37]

CONCLUSIONS

PHB and PVPh are easier to form hydrogen bonding according to their chemical structures if they were blended. The Fourier transform infrared spectroscopy analysis supports this conclusion. The
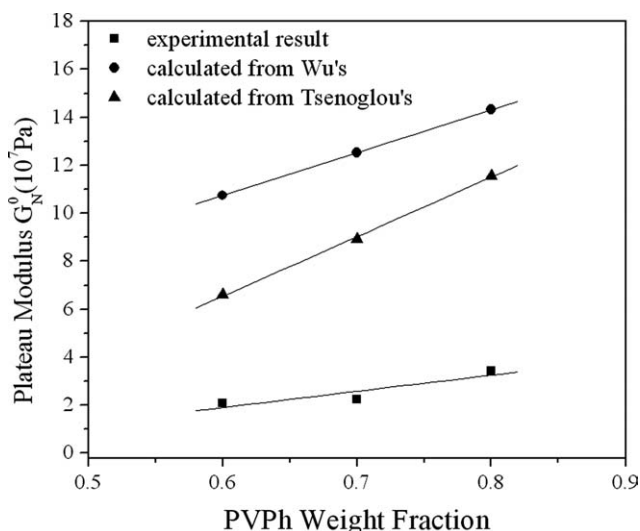
Figure 7 The rubber plateau modulus (G_N^0) versus PVPh weight fraction for the PHB/PVPh blends.

formation of hydrogen bonding in PHB/PVPh blends affects on the miscibility, crystallization and rheological behaviors directly. Firstly, when PHB content is less than 40%, the systems are completely homogeneous amorphous phase, which suggests that the addition of PVPh prevents the crystallization of PHB in the PHB/PVPh blends due to the presence of hydrogen bonding. Second, from the linear dynamic viscoelasticity of the miscible PHB/PVPh blends with compositions of 20/80, 30/70, 40/60, (w_t/w_t), the time-temperature superposition principle (TTS) is applicable in the experimental window, which suggests that the PHB/PVPh blends are miscible and there are not concentration fluctuations and dynamic heterogeneity in the blends. However, the Han plots are invalid since the curvatures of the plots in the terminal zone are much less than 2 obviously and become smaller with increasing of the PVPh content. This phenomenon is resulted from the presence of hydrogen bonding in the PHB/PVPh blends. The intensities of the whole hydrogen bonding (self-associated) of pure PVPh are greater than the ones of the whole hydrogen bonding (self-associated and the hydrogen bonding between hydroxyl group and ester group) of the blends and the intensities of the whole hydrogen bonding of the PHB/PVPh blends are enhanced with the increase of PVPh, therefore, it can be seen that the curvature of the Han plots in the terminal region of pure PVPh is much less than the PHB/PVPh blends obviously and the curvatures of the Han plots of the blends become smaller with increasing of the PVPh content. Third, the rubber plateau modulus (G_N^0) of the PHB/PVPh bends is much less than that estimated by Wu's and Tsenoglou's model. This is mainly attributed to the presence of the hydrogen bonding because Wu's and Tsenoglou's models do not take this into account. The presence of the hydrogen bonding between PHB and PVPh may confine the movement between the chain segments, reduce interchains convolution and block the entanglement between chains of the blends, which, in turn, decreases the rubber plateau modulus of the blends.

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