

결정화된 Poly(3-hydroxybutyrate)/Poly(*p*-vinylphenol) 블렌드에서 물리적겔화의 유변학적 측정

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Rheological Measurements of Physical Gelation in a Crystallized Poly(3-hydroxybutyrate)/Poly(*p*-vinylphenol) Blends

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Abstract: In our previous work, the miscibility and rheology behaviors of poly(3-hydroxybutyrate)/poly(*p*-vinylphenol) (PHB/PVPh) blends with homogeneous amorphous compositions had been studied. In this work, the rheological characteristics and physical gelation point have been investigated for the miscible PHB/PVPh blends with crystalline/amorphous compositions. The time sweep and frequency sweep of dynamic oscillatory experiment are discussed in details. The storage modulus G' and loss modulus G'' grow gradually along with the isothermal crystallization time, but the storage modulus G' exceeds the loss modulus G'' in the end. The physical gelation phenomena can be observed according to the power law method. In the flat region of loss tangent vs. angular frequency curves, the physical gelation point (t_g) of the PHB/PVPh 90/10 comes forth prior to the PHB/PVPh 80/20 during the liquid-solid transition process, which results mainly from the various isothermal crystallization rate of PHB component within PHB/PVPh blends.

Keywords: crystallization, dynamic rheology, poly(3-hydroxybutyrate), physical gelation point (t_g).

Introduction

During the last decades much attention have been focused on the development and investigation of crystalline polymer during the isothermal crystallization process, especially the liquid-solid transition, which can be beneficial to understand deeply the crystallization mechanism and accumulate application process data. On the crystallization course, the physical gelation phenomena can be observed for the reason of crystal appearing from a liquid to a solid state. Up to now, there are many reports on the liquid-solid transition, in existence many methods.¹⁻⁵ However, it was found that rheological measurements were a most sensitive tool to study the liquid-solid transition at the gel point,⁶⁻⁹ since the polymer structure cannot be destroyed by the dynamic rheological experiment and the linear dynamic viscoelasticity within the small stress can be sen-

sitive to the conformation change of the polymer.

As is well-known, the critical transition from liquid to solid state due to crystallization leads to the existence of physical gelation point. Therefore, it is important to determine what the gelation point of the process is. There are many ways to decide the gelation point by the rheology,¹⁰ but it is suggested that the power law method attributed by the contribution of Winter's effort,¹¹⁻¹⁶ that is the loss tangent at the gelation point is independent of the frequency, is extensive and valid. For all gelation systems at the gelation point, they found that for the dynamic oscillatory experiment:^{11,13,14}

$$G''(\omega)/G'(\omega) = \tan \delta = \tan(n\pi/2) \quad (1)$$

Where the G' , G'' , ω , δ and n refer to the storage modulus, loss modulus, angular frequency, loss angle and relaxation exponent, respectively. The gelation point is at an intermediate state between a liquid and a solid. It further evidences that when the system is in the vicinity of the gelation point, the loss tangent of dynamic oscillatory experiment is independent of

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angle frequency and has a fixed value. This law has been applied to determine the physical gelation point, for example, the gelation time, the gelation temperature, the gelation concentration and so on. This method had been approved to be convenient and valid for many polymer systems.¹⁷⁻²⁴

Poly(3-hydroxybutyrate) (PHB) is a crystalline polymer and poly(*p*-vinylphenol) (PVPh) is wholly amorphous.²⁵⁻²⁷ In our previous works,²⁸ it showed that the PHB/PVPh blends displayed a single-albeit broad-glass transition temperature (T_g), which indicates the miscibility of the blends at amorphous region. The powder WAXD experiments evidenced that, when PHB content is more than 60%, the PHB can crystallize in the blends and the crystallinity of PHB increases with the addition 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. The rheological behaviors of the homogeneous amorphous compositions of PHB/PVPh blends were studied in details. It is obvious that, If PHB in PHB/PVPh blend is crystallized, it will affect on rheological behaviors of the blends and physical gelation phenomena from the melt to solid can be observed as the result of the crystallization. In this work, the physical gelation phenomena caused by the PHB crystallization at higher PHB content (more than 80%) will be investigated by rheology method. The characteristics of the time sweep and frequency sweep in the dynamic oscillatory experiment are discussed in details.

Experimental

Materials and Blends Preparation. Poly(3-hydroxybutyrate) (PHB) with $M_w = 358000$ (T_g 3 °C, T_c 53 °C, T_m 165 °C) and $M_w/M_n = 1.24$ and poly(*p*-vinyl phenol) (PVPh) with $M_w = 20000$ (T_g 182 °C) 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 the most solvent. Next the blends were dried under vacuum at 65 °C for 7 days and annealed at 160 °C in a vacuum oven.

Instruments and Experiments. The polarizing optical microscopy (POM) (Nikon Eclipse E400) was employed to investigate crystal morphology of the samples. The samples were melted at 180 °C for 2 min and then transferred as quickly as possible to another hot stage (Instec STC200) at a

prefixed 130 °C for isothermal crystallization. The morphology and radius of the spherulite were recorded with time.

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 ranged from 0.1 to 100 rad/s with stress from 10 pa to 1500 pa at 130 °C. Storage modulus G' and loss modulus G'' as a function of angular frequency or crystallization time were obtained. The samples were firstly melted at 180 °C for 2 min and quenched to the crystallization temperature 130 °C, then carried out the dynamic oscillatory measurements as quickly as possible.

Results and Discussion

It was found in our previous works that the PHB/PVPh blends displayed a single-albeit broad-glass transition temperature (T_g), which indicated the blends were miscible for all compositions at amorphous region.²⁸ When PHB content is less than 60% in the blends, the blend systems are completely homogeneous amorphous phase. The linear dynamic viscoelasticity behaviors and time-temperature superposition principle of the blend systems within completely homogeneous amorphous phase were studied in details.²⁸ When PHB content is more than 60% in the blends, the PHB is able to crystallize and the crystallinity of PHB increases with the addition of PHB contents shown in the DSC and WAXD results of our previous report.²⁸ It is obvious that, if PHB in PHB/PVPh blend is crystallized, it will affect on rheological behaviors of the blends and physical gelation phenomena from the melt to solid might be occurred as the result of the crystallization. Therefore, in this work, the PHB/PVPh systems with compositions of 100/0, 90/10 and 80/20 were selected to study the rheological behaviors and the physical gelation point of liquid-solid transition.

PHB is a crystalline polymer and PVPh is wholly amorphous polymer. PHB is able to form crystal and its melt point is about 165 °C. Our main purpose is to research the rheological characteristic and the physical gelation point of the miscible PHB/PVPh blending samples resulted from the PHB crystallization. PHB may crystalline when temperature is below its melt point. The crystallization rate becomes larger with the decrease of crystallization temperature. The physical gelation phenomena resulted from the crystallization cannot be

investigated obviously by the rheological measurement when the crystallization temperature is very low. Therefore, we choose 130 °C for all compositions to study the physical gelation point resulted from the crystallization.

The angular frequency sweeps of the samples with crystallization time were carried out for crystallization solidification processes with isothermal crystallization temperature of 130 °C, as shown in Figures 1(a)-(c) (The sweeping process are operated from high to low frequency). The total measuring time for each frequency sweep curve from 100 to 0.1 rad/s of angular frequency is about 70 s. During isothermal crystallization in dynamic angular frequency sweep experiment, the crystallization time, 7 s, 157, etc., is not the real one and that is the beginning sweep time each time from the melt to solid. It is researched to see the rheological characteristic and the trend from the melt to solid, and it does not matter with the time precisely. This is to see the physical gelation point of the samples, resulted from the crystallization, not the crystallization process itself for aim, so the G' data for “7 s” or other crystallization time can be used to investigate the gelation phenomena. It can be found that the storage modulus G' of three samples behave the same trend with the angular frequency. Before PHB crystallizes from the melt, the storage modulus G' of the blend systems decreases linearly with decreasing of the angular frequency and behaves the classical linear dynamic viscoelasticity behaviors as following equation:

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

Where G' , ω , J_e^0 , and η_0 is storage modulus, frequency, steady-state shear compliance and zero steady-state shear viscosity, respectively. At the initial crystallization stage, the storage modulus G' decreases firstly and then increases with decreasing of angular frequency. During dynamic sweeping process, the PHB crystals increase continuously and the storage modulus of samples increases with the sweeping time, which results in the deviation from the classical linear dynamic viscoelasticity till the end. It indicates that the transition from liquid to solid resulted from PHB crystallization has occurred in practice during this process. With the further crystallization, the storage modulus G' also deviates from the classical linear dynamic viscoelasticity much more and is independent of the angular frequency in the end, which indicates the sample behaves the property of solid state much more. It suggests that the rheological characteristic have been changed resulted from the crystallization and the physical gelation phenomena from

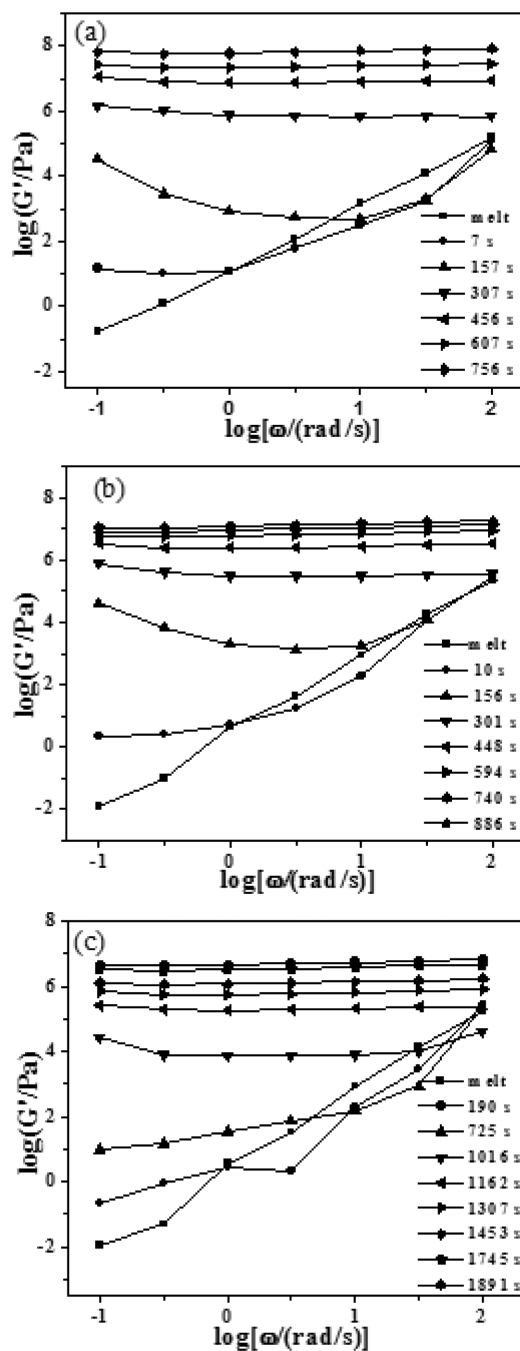


Figure 1. Storage modulus G' vs. angular frequency curves for different crystallization time during isothermal crystallization at 130 °C in the dynamic angular frequency sweep experiment: (a) PHB/PVPh 100/0 (W/W); (b) 90/10; (c) 80/20.

the liquid to solid state can be observed. Then it can also be found that the beginning time, where the storage modulus G' is independent of the angular frequency, is different for three samples and behaves much longer with the addition of PVPh content. The transition from liquid to solid state becomes more

uneasy with the PVPh content addition, and since the addition of PVPh restrains from the PHB crystallization. At the same time, the loss tangent vs. angular frequency curves from the liquid to solid process have also been investigated, as shown in Figure 2.

It is noted that it is necessary to estimate the characteristic relaxation time when performing the dynamic frequency sweep of rheology. In our previous report,²⁸ it indicated that the

miscible amorphous system of the PHB/PVPh blends was formed (PHB content less than 40% within the blends) and the time-temperature superposition principle was applicable due to the presence of hydrogen bonding. As shown in the master curves (frequency sweep of dynamic rheology), it can be inferred that the angular frequency is more than 1 rad/s at the relaxation time point. In this paper, as a continual work, the rheological characteristics and physical gelation point are investigated for the miscible PHB/PVPh blends with crystalline/amorphous compositions (PHB content more than 80%). However, the relaxation time of blends in this paper when melting should be similar to the relaxation time of blends in our previous report (amorphous system). In addition, in this paper, the smallest time for frequency sweep test is 7 s. Therefore, the characteristic relaxation time should be shorter than total time for frequency sweep tests.

Figures 2(a)-(c) show the relationships of loss tangent and angular frequency for PHB/PVPh blend systems with different compositions. It can be seen that the loss tangent along with angular frequency in the terminal zone becomes flat after a certain crystallizing time. The flat regions are located at the time range of 456-607 s, 594-740 s and 1453-1745 s for the PHB/PVPh blends with compositions of 100/0, 90/10 and 80/20, respectively. It has been confirmed the gelation point is at an intermediate state between a liquid and a solid. According to the power law method put forward by Winter *et al.*,^{11,13,14} when the system is in the vicinity of the gelation point, the loss tangent of the dynamic oscillatory experiment is independent of the angular frequency. Therefore, it indicated that the physical gelation point should take place at the different time point for various samples. It is reasonable because the addition of PVPh prevents the PHB from crystallizing in the PHB/PVPh blends, and the different composition behaves different crystallization rate, as shown in Figure 3. In our previous report,²⁸ it indicated that the miscible amorphous system of the PHB/PVPh blends was formed (PHB content less than 40% within the blends) and the PHB crystallization morphology mainly depended on the blend composition. As shown in Figure 3, it shows the spherulite morphology and growth radius vs. the isothermal crystallization time for PHB/PVPh blends at 130 °C using polarized light optical microscopy. The distorted banding spherulite morphologies are present at the all samples. With the increase of PHB content within the PHB/PVPh blends, the banded spherulite morphology is still formed but the banding is distorted to highly zigzag irregularity. The slope of linear-like curves refers to the growth rate of PHB spherulites, as

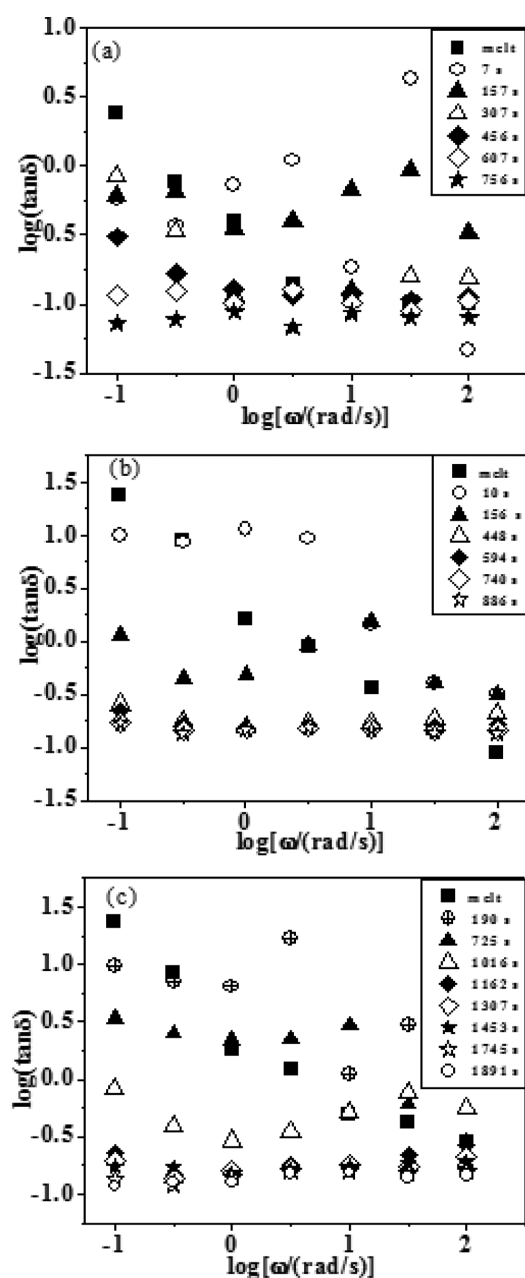


Figure 2. Loss tangent vs. angular frequency curves for different crystallization time from liquid to solid state at 130 °C: (a) PHB/PVPh 100/0 (W/W), (b) 90/10, (c) 80/20.

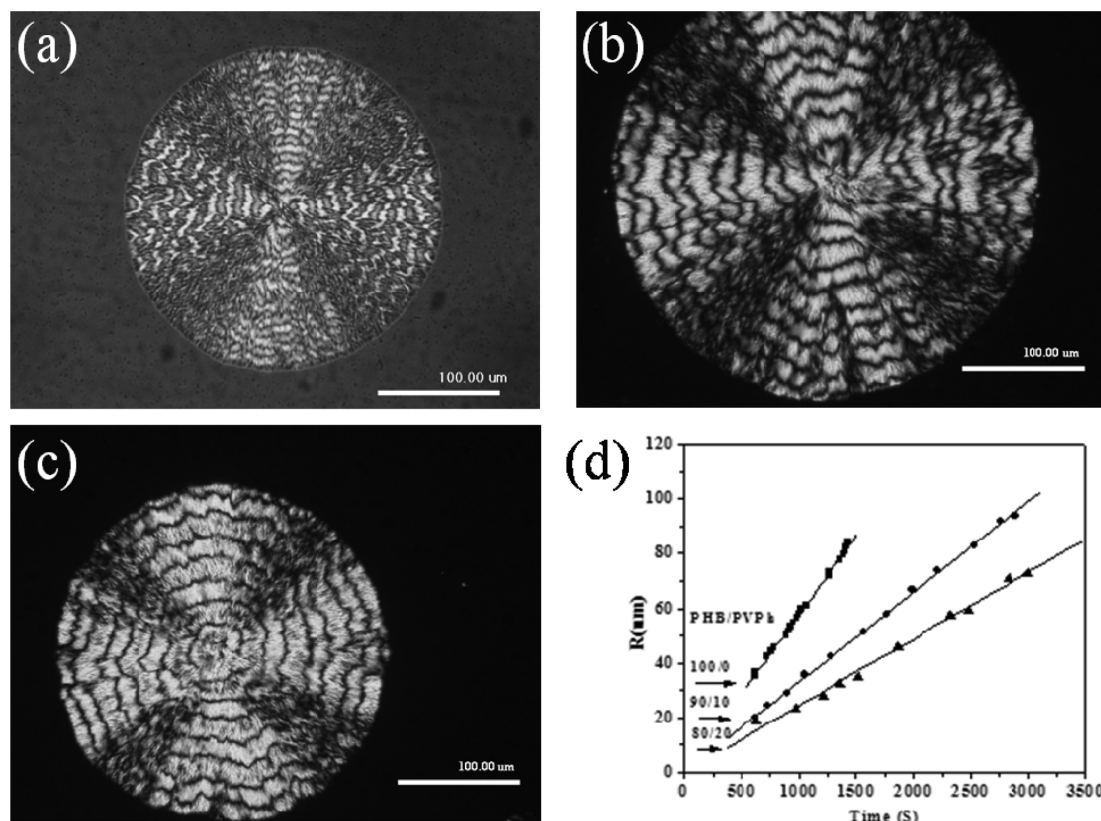


Figure 3. Spherulite morphology of PHB/PVPh blends at 130 °C using polarized light optical microscopy: (a) PHB/PVPh 100/0 (W_t/W_l) with crystallization for 2000 s; (b) 90/10 with crystallization for 4750 s; (c) 80/20 with crystallization for 5375 s, and spherulite growth radius vs. the isothermal crystallization time (d).

shown in Figure 3(d). The growth rate of PHB spherulites decreases obviously with increasing of PVPh content in the PHB/PVPh blends. The physical gelation point here is mainly determined by the PHB crystallization process. Once a fixed size of PHB crystal is present, it indicates that the physical gelation point during crystallization process is obtained. As shown in Figure 3, when the blends reach the same crystal size, it will cost more time for the polymer blend with higher PVPh content. Therefore, it indicates that the addition of PVPh leads to the delay of the gelation point during isothermal crystallization process.

To further determine the gelation time at the gelation point of PHB/PVPh 90/10 and PHB/PVPh 80/20, the dynamic time sweep with different frequency experiment have been carried out, as shown in Figure 4 and Figure 5.

During the liquid-solid transition process as a result of isothermal crystallization, as shown in Figure 4, it can be seen that through a induction period, the storage modulus G' and loss modulus G'' start to grow strongly with the crystallization time going on, but soon the storage modulus G' exceeds the

loss modulus G'' till the end of the operation. At the same time, the storage modulus G' and loss modulus G'' approach to each other in the end and this rule all emerges for different angular frequency. From then it is concluded that the crystallization have led to the change of storage modulus G' and loss modulus G'' . Therefore, it shows that it is inevitable to take place the physical gelation phenomena and appear the gelation point of samples during the liquid-solid transition.

On the bases of power law method (the gelation point is determined from the loss tangent independence of frequency), the gelation point is determined accurately, as shown in Figure 5, where it is the gelation point that the curves pass through a common point for a certain crystallization time. It can be seen that the value of loss tangent starts to decrease strongly when reaching a certain crystallization time. This trend can be attributed to the change of storage modulus G' and loss modulus G'' in the PHB crystallization process. During the liquid-solid transition, the gelation time (t_g), which is the crossover of the loss tangent vs. crystallization time curves with low angular frequency, is about 700 s for PHB/PVPh 90/10 and about

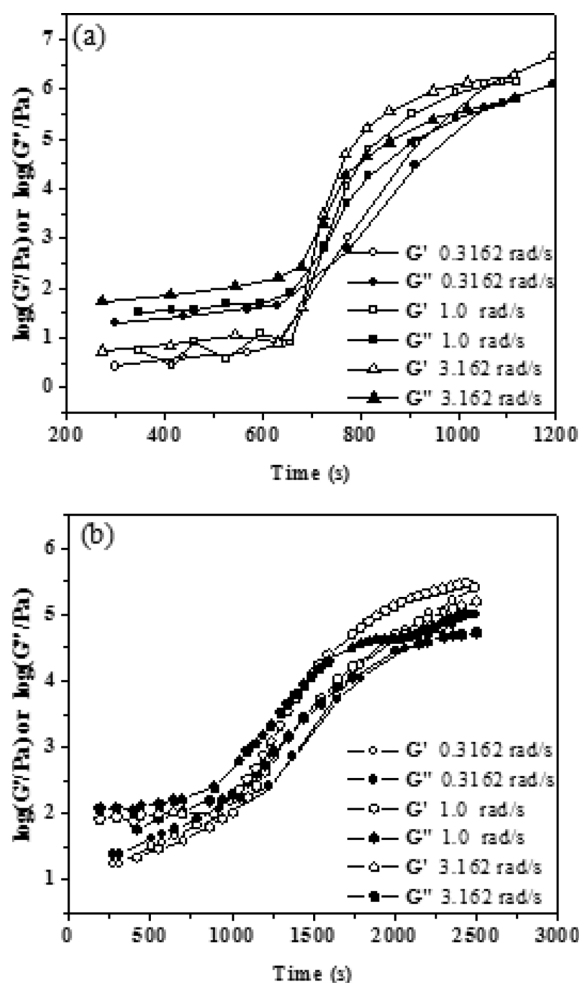


Figure 4. Storage modulus G' and loss modulus G'' vs. crystallization time curves for different angular frequency from liquid to solid state at 130 °C in the dynamic time sweep experiment: (a) PHB/PVPh 90/10 (W/W); (b) 80/20.

1540 s for 80/20. This differential result mainly from the different isothermal crystallization rate, as shown in Figure 4.

As a matter of fact, the blend of PHB with PVPh is miscible^{25,27-33} and the miscibility, crystallization and morphology of this system have been widely affected by intermolecular hydrogen bonding interaction. 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. Therefore, the addition of PVPh prevents the PHB from crystallizing in the PHB/PVPh blends and results in a reduction of the crystallization rate. As a result, it can be investigated that the gelation point (t_g) of the PHB/PVPh 90/10 takes place prior to the PHB/PVPh 80/20 during the physical gelation phenomena process. In addition, PHB is a crystalline

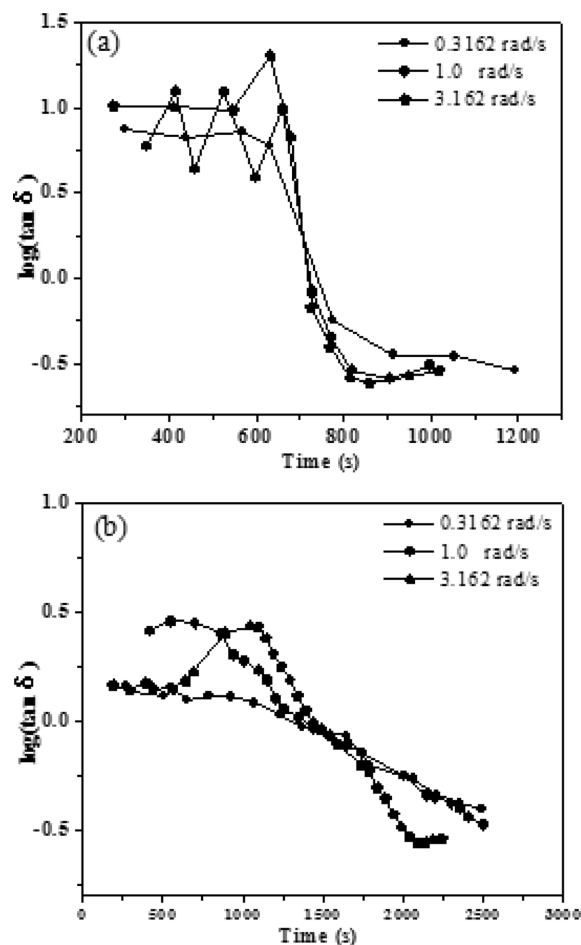


Figure 5. Loss tangent vs. crystallization time curves for different angular frequency from liquid to solid state at 130 °C in the dynamic time sweep experiment: (a) PHB/PVPh 90/10 (W/W); (b) 80/20.

polymer and PVPh is wholly amorphous polymer. When they are mixed together, it has been evidenced that the PHB/PVPh blends displayed a single albeit broad-glass transition temperature (T_g), which indicates the blends are miscible in amorphous region. As a classic blend sample, it has been reported in many studies,^{25,27,28} regarding to its miscibility and crystallization. It indicated that the addition of PVPh prevented crystallization of PHB in the blends, of course, it meant that PVPh decreased the crystalline melting temperature and degree of crystallinity of PHB in the blends. Our main purpose is to research the rheological characteristic and the physical gelation point of the miscible PHB/PVPh blending samples resulted from the crystallization. So the physical gelation of the blend is also correlated with degree of crystallinity of the samples. With the increase of PVPh content in the blends, the degree of crystallinity of PHB within blends will become decreased, but the physical gelation point in this paper is deter-

mined mainly by the PHB crystallization. Therefore, the decrease of degree of crystallinity is also destined to prolong the physical gelation point.

There is note that the final values of G' in Figure 4 are different from that in Figure 1. We have checked the measurement condition again and the two measurement condition is identical indeed. This differential may be resulted from the different measurement mode because the crystallization is a very complicated process, for example, the shear process may affect the crystallization process slightly. The corresponding discussion in detail will be investigated in the next work. However, this differential does not affect our purposes and results in this paper. This differential between two figures is very limited and the change trend of each figure is obvious and rationed. Therefore, we are yet able to obtain the conclusion that the change of physical gelation point mainly resulted from different crystallization rate for various blend compositions.

Conclusions

The PHB/PVPh blends are completely homogeneous amorphous phase when PHB content is less than 40% in the blends, while the PHB can crystallize to form crystalline/amorphous state when PHB content is more than 60% in the blends. The rheology behaviors of the blends change dramatically with the appearance of physical gelation point due to isothermal crystallization. According to the dynamic oscillatory experiment of the blends during isothermally crystallization process, the storage modulus G' and loss modulus G'' increase gradually with the crystallization time, and the storage modulus G' exceeds the loss modulus G'' in the end. The flat region in the loss tangent vs. angular frequency curves appears associated with the gelation point. According to the power law method, the physical gelation point has been determined due to the loss tangent at the physical gelation point being independent of the frequency. It shows that the physical gelation points (t_g) of PHB/PVPh blends increases with the addition of PHB contents because the isothermal crystallization rate of the PHB decreases with the increase of PVPh contents.

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References

1. M. Schmidt and W. Burchard, *Macromolecules*, **14**, 370 (1981).
2. E. M. Valles and C. W. Macosko, *Macromolecules*, **12**, 673 (1979).
3. C. Allain and C. Amiel, *Phys. Rev. Lett.*, **56**, 1501 (1986).
4. S. V. Muzumdar and L. J. Lee, *Polym. Eng. Sci.*, **31**, 1647 (1991).
5. E. M. Valles and C. W. Macosko, *Macromolecules*, **12**, 521 (1979).
6. P. J. Philips, *Rep. Prog. Phys.*, **53**, 549 (1990).
7. W. J. Yoon, H. S. Myung, B. C. Kim, and S. S. Im, *Polymer*, **41**, 4933 (2000).
8. N. E. Allison, M. D. Nicole, C. K. Stephanie, and R. W. Newell, *Biomacromolecules*, **12**, 2610 (2011).
9. F. Y. Liu, F. Y. Li, G. H. Deng, Y. M. Chen, B. Q. Zhang, J. Zhang, and C.Y. Liu, *Macromolecules*, **45**, 1636 (2012).
10. C. W. Macosko, *Brit. Polym. J.*, **17**, 239 (1985).
11. F. Chambon and H. H. Winter, *Polym. Bull.*, **13**, 499 (1985).
12. C. Schwittay, M. Mours, and H. H. Winter, *Faraday Discuss.*, **101**, 93 (1995).
13. H. H. Winter and F. Chambon, *J. Rheol.*, **30**, 367 (1986).
14. F. Chambon and H. H. Winter, *J. Rheol.*, **31**, 683 (1987).
15. J. C. Scanlan and H. H. Winter, *Macromolecules*, **24**, 47 (1991).
16. M. Mours and H. H. Winter, *Macromolecules*, **29**, 7221 (1996).
17. K. T. Nijenhuis and H. H. Winter, *Macromolecules*, **22**, 411 (1989).
18. Y. G. Lin, D. T. Mallin, J. C. W. Chien, and H. H. Winter, *Macromolecules*, **24**, 850 (1991).
19. C. Michon, G. Cuvelier, and B. Launay, *Rheol. Acta*, **32**, 94 (1993).
20. K. Boutahar, C. Carrot, and J. Guillet, *J. Appl. Polym. Sci.*, **60**, 103 (1996).
21. B. D. Chin and H. H. Winter, *Rheol. Acta*, **41**, 265 (2002).
22. K. M. Schultz, A. D. Baldwin, K. L. Kiick, and E. M. Furst, *Macromolecules*, **42**, 5310 (2009).
23. A. K. M. Norman and J. L. Brian, *Macromolecules*, **44**, 3548 (2011).
24. S. Sanwlani, P. Kumar, and H. B. Bohidar, *J. Phys. Chem. B*, **115**, 7332 (2011).
25. W. P. Chae, Z. C. Xing, Y. J. Kim, H. S. Sang, M. W. Huh, and I. K. Kang, *Polym. Korea*, **35**, 210 (2011).
26. K. H. Jeong and Y. J. Kim, *Polym. Korea*, **30**, 512 (2006).
27. L. A. Belfiore, C. Qin, E. J. Ueda, and A. T. N. Pires, *J. Polym. Sci. Polym. Phys. Ed.*, **31**, 409 (1993).
28. G. Z. Ding, K. Cui, and J. P. Liu, *J. Appl. Polym. Sci.*, **122**, 617 (2011).
29. P. Iriondo, J. J. Iruin, and M. J. Fernandez-Berridi, *Macromolecules*, **29**, 5605 (1996).
30. P. Iriondo, J. J. Iruin, and M. J. Fernandez-Berridi, *Polymer*, **36**, 3235 (1995).
31. P. X. Xing, L. S. Dong, Y. X. An, and Z. L. Feng, *Macromolecules*, **30**, 2726 (1997).
32. Y. He, J. C. Li, X. T. Shuai, and Y. S. Inoue, *Macromolecules*, **34**, 8166 (2001).
33. J. C. Li, Y. He, and Y. S. Inoue, *J. Polym. Sci., Part B: Polym. Phys.*, **40**, 2736 (2002).