

INVESTIGATION ON THE GELATION BEHAVIOR OF BIODEGRADABLE POLY(BUTYLENE SUCCINATE) DURING ISOTHERMAL CRYSTALLIZATION PROCESS*

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Abstract The early stage of polymer crystallization may be viewed as physical gelation process, *i.e.*, the phase transition of polymer from liquid to solid. Determination of the gel point is of significance in polymer processing. In this work, the gelation behavior of poly(butylene succinate) (PBS) at different temperatures has been investigated by rheological method. It was found that during the isothermal crystallization process of PBS, both the storage modulus (G') and the loss modulus (G'') increase with time, and the rheological response of the system varies from viscous-dominated ($G' < G''$) to elastic-dominated ($G' > G''$), meaning the phase transition from liquid to solid. The physical gel point was determined by the intersection point of loss tangent curves measured under different frequencies. The gel time (t_g) for PBS was found to increase with increasing crystallization temperature. The relative crystallinity of PBS at the gel point is very low (2.5%–8.5%) and increases with increasing the crystallization temperature. The low crystallinity of PBS at the gel point suggests that only a few junctions are necessary to form a spanning network, indicating that the network is “loosely” connected, in another word, the critical gel is soft. Due to the elevated crystallinity at gel point under higher crystallization temperature, the gel strength S_g increases, while the relaxation exponent n decreases with increasing the crystallization temperature. These experimental results suggest that rheological method is an effective tool for verifying the gel point of biodegradable semi-crystalline polymers.

Keywords: Poly(butylene succinate); Gelation process; Rheological analysis.

INTRODUCTION

Polymeric gel is a three-dimensional network, formed by flexible molecular chains either through chemical cross-linking (chemical gel) or physical phase transformation (physical gel)^[1]. In chemical gelation, small molecules connect by covalent bonds into large clusters, and the gel point (GP) is established when the first molecular cluster has grown to infinite size, *i.e.*, to the size of the sample. Physical gel is a percolated three-dimensional (3D) network, in which the macroscopic connectivity arises from physical interactions. The long-range connectivity can be attributed to various forces, such as van der Waals, hydrogen bonds and electrostatic interactions, induced by cross-linking formation due to the presence of physical aggregates, crystals or fillers. Crystallizing polymers show a typical example of physical gelation behavior due to formation of crystals when undergoing a liquid-solid transition. During this process, crystalline order slows down the

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molecular motions while increasing the connectivity between molecules. Motions of groups of molecules correlate over considerable distance (growing correlation length) and the state at which the correlation length diverges is defined as the physical gel point^[2–4]. However, this gel point generally occurs at very low crystallinity. It was found that the crystallinity at gel point of PP was about 3%^[5, 6]. Similar result has been reported in PE system^[7]. All these investigations indicate that the gelation process for most of semi-crystalline polymers occurs at the early stage of crystallization. That is to say, only a few junctions are necessary to form a sample spanning network at the gel point, and the critical gel is soft.

Knowing of the GP is very important for crystalline polymer processing practice, because the characteristic crystallization time for each material can be tailored to the given molding circumstances or shaping has to occur before GP while the polymer can still flow and stress can relax to zero. In addition, exact knowledge of GP may allow for processing in the critical gel state (GP) and novel techniques of gel processing can be developed^[8, 9]. So far, many methods for determination of GP including dynamic and static light scattering^[10], permeability^[11], nuclear magnetic resonance^[12], differential scanning calorimetry (DSC)^[13], infrared spectroscopy^[14] and fluorescence spectroscopy^[15] have been developed. However, with development of rheology theory and techniques, the viscoelastic functions such as dynamic storage modulus G' , loss modulus G'' and loss tangent $\tan\delta$ measured through dynamic shear tests are found to be very sensitive to the structural changes during the formation of a polymeric gel and found experimentally that critical gels exhibited simple relaxation behavior following a power-law relaxation shear modulus^[16–18]:

$$G(t) = S_g t^{-n} \quad (1)$$

where S_g is the gel strength and n is the relaxation exponent. The above equation can be expressed in terms of storage modulus G' and loss modulus G'' :

$$G'(\omega) = S_g \omega^n \Gamma(1-n) \cos(n\pi/2) \quad \text{for } \omega < \omega_0 = 1/\lambda_0 \quad (2)$$

$$G''(\omega) = S_g \omega^n \Gamma(1-n) \sin(n\pi/2) \quad (3)$$

where ω is the angular frequency, and Γ is the gamma function. According to Eqs. (2) and (3), $\tan\delta$ can be expressed by

$$\tan\delta = G''/G' = \tan(n\pi/2) = \text{const} \quad (4)$$

where δ is the loss angle. At the gel point, $\tan\delta$ is independent of angular frequency, which provides the most reliable method for determining the gel point. So, the dynamic rheology becomes a powerful tool to monitor gelation and microstructural changes in polymer materials^[19] and has been extensively used to study the viscoelastic behavior of polymer gels near the sol-gel transition and determination of GP^[20–27].

In the present work, the rheological method was used to investigate the gelation behavior of isothermally crystallizing poly(butylenes succinate) (PBS). Emphasis was made on finding a correlation between kinetic characteristics (gel times, crystallization rates) and structural parameters of the critical gel (gel stiffness, relaxation exponent, crystallinity). The results are useful for the melt processing of PBS.

EXPERIMENTAL

Materials

Poly(butylene succinate) (PBS) with $M_w = 1.15 \times 10^5$, $M_n = 8.01 \times 10^4$ and PDI = 1.44 (GPC) was supplied from Technical Institute of Physics and Chemistry of the Chinese Academy of Sciences.

Sample Preparation and Characterization

The dynamic rheological properties for isothermally crystallizing PBS were determined using a strain-controlled Advanced Rheometric Expansion System (ARES, Rheometric Scientific, NJ) equipped with parallel plate geometry (diameter of 25 mm) under N_2 ambient. The sample was held at 150°C for 5 min to erase thermal and mechanical history, and then rapidly cooled down to the designed temperature to monitor the development of the

loss and storage modulus at preset angular frequency. The samples used for rheological measurement were prepared by hot compression as a cylinder with diameter of 25 mm and thickness of 1 mm at 150°C and 10 MPa.

Differential scanning calorimetric measurement (DSC) was performed on a Perkin-Elmer DSC-7. The calibration for temperature and melting enthalpy was performed using indium as the standard. Approximately 2–3 mg of the samples were sealed in aluminum pans and used for measurements. The sample was first heated to 150°C and kept for 5 min to erase thermal history, and then rapidly cooled down to the designed temperature and kept till the heat flow did not change with the crystallization time. The whole process was executed under N₂ atmosphere.

RESULTS AND DISCUSSION

Evolution of Storage Modulus G' and Loss Modulus G'' with Gelation Process

The evolution of G' and G'' with time during crystallization process of PBS at 90°C for six different frequencies is shown in Fig. 1. A long induction period is obvious before the modulus starts to increase sharply, indicating that the PBS melt is homogeneous after thermal treatment^[21]. At the beginning of the experiment, the storage modulus G' is smaller than the corresponding loss modulus G'' . After a long induction period, G' and G'' begin to grow strongly and soon G' exceeds G'' to dominate the crystallization process, indicating that G' and G'' are very sensitive to the structural changes inside the material during PBS isothermal crystallization and the sample gradually shifts from viscoelastic liquid to solid. Furthermore, both G' and G'' increase with the enhancement in the angular frequency.

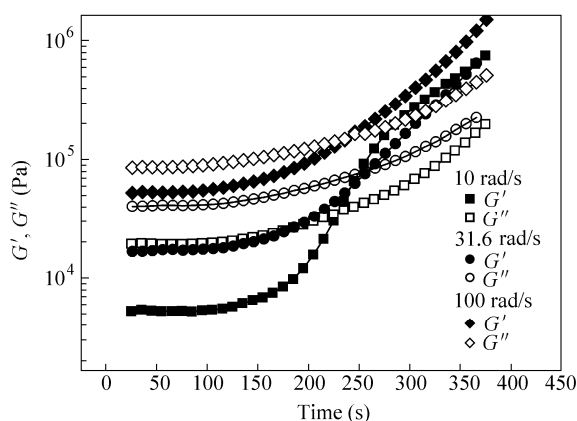


Fig. 1 Evolution of visco-elasticity with time at different frequencies for PBS crystallized at 90°C

Evolution of Storage Modulus G' with Angular Frequency during Gelation Process

Based on the viscoelasticity theory, the dynamic storage modulus and loss modulus for viscoelastic liquids can be expressed by the following expressions:

$$G'(\omega) \propto \omega^2, \quad G''(\omega) \propto \omega \quad (5)$$

Both the plot of $\lg G'$ against $\lg \omega$ and that of $\lg G''$ against $\lg \omega$ are linear in the frequency-terminal region. The slopes of $\lg G'$ and $\lg G''$ are 2 and 1, respectively. Figure 2 shows the variation of storage modulus G' with angular frequency at different crystallization times. As the crystallization proceeds, the slope of the storage modulus G' curves is found to gradually shift from 2 to lower values and a flat line appears, indicating that the sample gradually shifts from viscoelastic liquid to solid due to the formation of cluster, skeleton, networks, or other ordered crystal structures. This is a typical rheological features of polymer gelation^[17, 18, 21]. Therefore, in the present study, rheological method is sensitive and suitable to characterize the gel point of PBS during isothermal crystallization.

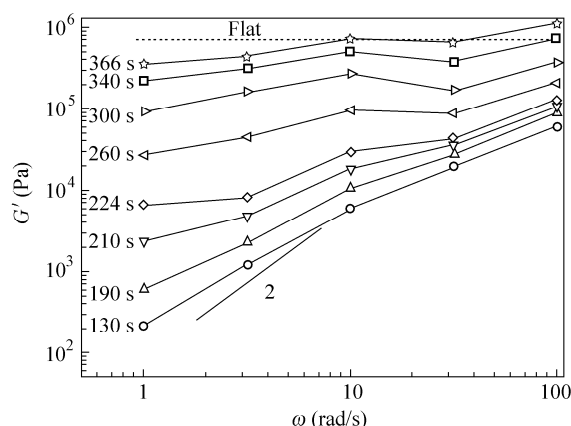


Fig. 2 Evolution of the storage modulus G' with angular frequency ω during isothermal crystallization for PBS at 90°C

Evolution of Loss Tangent $\tan\delta$ and Determination of the Physical Gel Point during Isothermal Crystallization

According to Eq. (4), the angular frequency independence of the loss tangent $\tan\delta$ gives access to determination of the gel point. Figure 3 shows the evolution of $\tan\delta$ with crystallization time at different frequencies for PBS crystallized at 90°C. At the beginning of crystallization experiment, the low-frequency $\tan\delta$ is higher than that of the high-frequency. After a long induction time, the $\tan\delta$ starts to decrease and the low-frequency $\tan\delta$ drops faster than the corresponding high-frequency $\tan\delta$. The intersection point, correlated to the critical gel point as given by Eq. (4), can be observed. The gel time t_c and the corresponding $\tan\delta$ are 226 s and 1.17, respectively. The critical gel relaxation exponent n is 0.55, which is calculated from the gel point by using Eq. (4). The gel time t_c and the relaxation exponent n for PBS crystallized at 87°C, 88°C, 89°C and 90°C were evaluated, and their variation with crystallization temperature is shown in Fig. 4. It is observed that the t_c increases with the crystallization temperature, indicating that the liquid-to-solid transition is delayed at high crystallization temperature. Figure 4 also shows that the critical gel becomes harder with the increase of crystallization temperature, which is reflected by the decrease of n values^[6]. The result is contradictory to that of the isotactic polypropylene (*iPP*) reported previously, which becomes softer and more fragile at high crystallization temperature, *i.e.* n increase with the crystallization temperature^[6]. Crystallization often is viewed as two ongoing processes. First is the radial growth of aggregates and fibrous “strands” governed by radial growth rate. This is responsible for interconnected network formation (gelation) and is manifested experimentally in t_c . The second

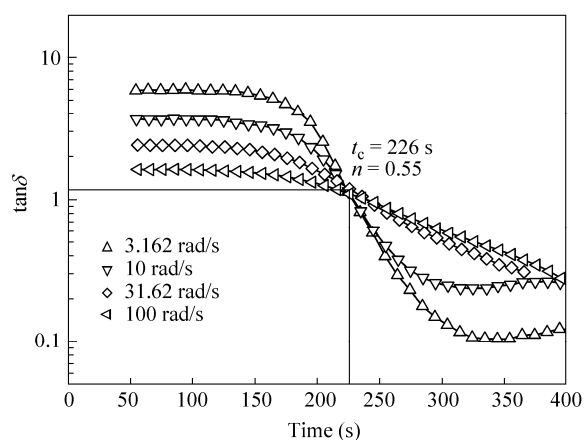


Fig. 3 Evolution of $\tan\delta$ of PBS with crystallization time at 90°C

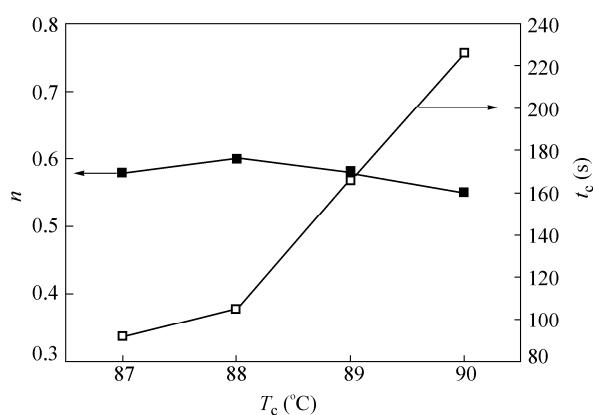


Fig. 4 Variation of critical gel relaxation exponent n and gel time t_c with crystallization temperature

is internal crystallization inside the aggregates (through making them volume-filled with ordered crystals) governed by the internal crystallization rate and is manifested experimentally through Avrami time t_A . The competition of these processes may be evaluated by the ratio of t_c/t_A . t_A can be calculated by $t_A = K^{-1/N}$ [6]. Where K is the isothermal crystallization rate constant and N is Avrami exponent. The values of K and N calculated by isothermal crystallization Avrami equation at different crystallization temperatures are listed in Table 1. The t_c/t_A as a function of crystallization temperature is shown in Fig. 5. The values of t_c/t_A increase with crystallization temperature, *i.e.*, radial growth rates increase faster than internal crystallization rates for PBS with the enhancement of crystallization temperature, as a result the critical gel becomes harder at high crystallization temperatures.

Table 1. The values of N , K and t_A of PBS at different crystallization temperatures

T_c (°C)	N	K	$t_A = K^{-1/N}$ (s)
87	2.86	0.0108	292.2
88	2.69	0.0101	331.2
89	2.68	0.0051	430.2
90	2.70	0.0026	544.2

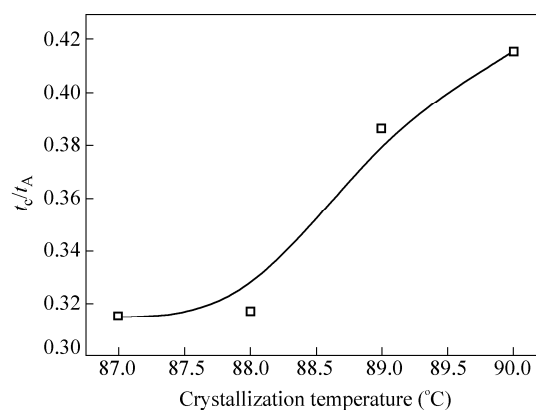


Fig. 5 Characteristic time ratio (t_c/t_A) at the gel point versus crystallization temperature for PBS

Dependence of Gel Strength S_g on the Crystallization Temperature

The gel strength S_g in Eq. (1) is also an important parameter for characterizing polymer physical gels. According to Eqs. (2), (3) and (4), Eq. (6) can be obtained:

$$G'(\omega) = G''(\omega)/\tan(n\pi/2) = S_g \omega^n \Gamma(1-n) \cos(n\pi/2) \quad (6)$$

G' and $G''/\tan(n\pi/2)$ will cause an intersection at the gel point in the plots of the G' and $G''/\tan(n\pi/2)$ as a function of crystallization time (Fig. 6). All intersection points appear at the vicinity of the gel point of $t_c = 226$ s, which is consistent with that acquired by using the frequency independence of $\tan\delta$ in Fig. 3. By using the values of G' at intersection points and Eq. (6), the calculated value of S_g is around 7.1×10^3 Pa s^{*n*} for PBS crystallized at 90°C. Liu found that n is 0.75 and S_g is 770 Pa s^{*n*} for the carbon nano-tube/polycarbonate composite^[21]. Meanwhile, Pogodina reported that n is 0.65 and S_g is 7.5×10^3 Pa s^{*n*} for *i*PP during isothermal crystallization at 145°C^[6]. The above results indicate that the present data related with n and S_g of PBS is reasonable and reliable.

The effect of crystallization temperature on S_g is shown in Fig. 7. The S_g increases with the rise of crystallization temperature, indicating that the gel becomes harder. This is in consistence with the results reflected in n values.

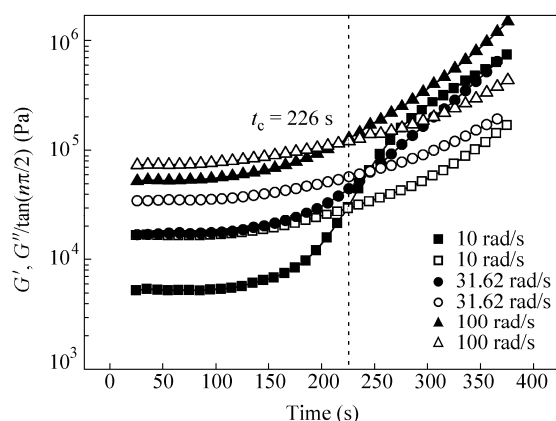


Fig. 6 Plots of G' and $G''/\tan(n\pi/2)$ against crystallization time of PBS for different frequencies. The filled symbols represent G' , while the hollow symbols represent $G''/\tan(n\pi/2)$.

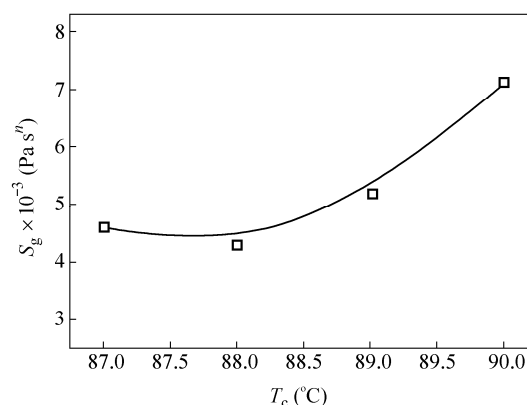


Fig. 7 Effect of crystallization temperature of PBS on S_g .

Variation of Crystallinity during the Gelation Process

Stress and strain strongly affect the crystallization behavior of polymers. However, Winter indicated that a low strain does not apparently affect the crystallization behavior of polymers^[6]. In addition, the crystallization kinetics tested by DSC is in good agreement with that tested by rheological method at low crystallinity^[8]. Generally, for a semi-crystalline polymer, the physical gelation process occurs at a very low crystallinity during isothermal crystallization. The crystallinity of *i*PP merely reaches about 3% when the gel state is achieved^[6]. In the current study, the experiment was executed at a small strain of 3%, which does not affect the crystallization behavior of PBS. Therefore, the crystallinity at gel point of PBS was directly read from the DSC data. Figure 8 shows the DSC heat flow curves and the relative crystallinity variation of PBS crystallized at 90°C. It can be clearly seen that the crystallinity of PBS is found to be around 8.5% when the gel state is reached ($t_c = 226$ s). The variation of crystallinity with crystallization temperature at the gel point is shown in Fig. 9. Obviously, although the crystallinity at gel point increases with the crystallization temperature, all of them are very low (about 2.5%–8.5%), suggesting that only a few junctions are necessary to form a spanning network and the network is “loosely” connected, or the critical gel is soft.

The dependence of G' , G'' and $\tan\delta$ on the crystallinity at angular frequency of $\omega = 10$ rad/s as an example is shown in Fig. 10. The slope of G' , G'' , and $\tan\delta$ show a jump change at gel point, indicating that the change of G' , G'' and $\tan\delta$ with crystallinity is closely related with the gel point.

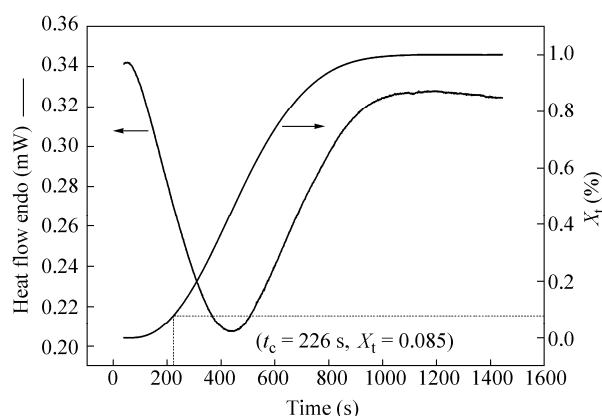


Fig. 8 DSC curves of PBS and the variation of relative crystallinity with crystallization time at 90°C

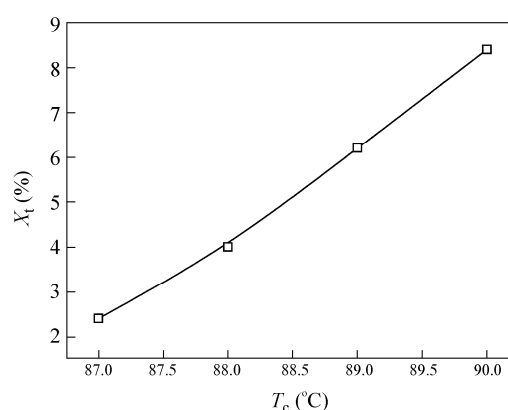


Fig. 9 Crystallinity at the gel point for PBS isothermally crystallized as a function of crystallization temperature

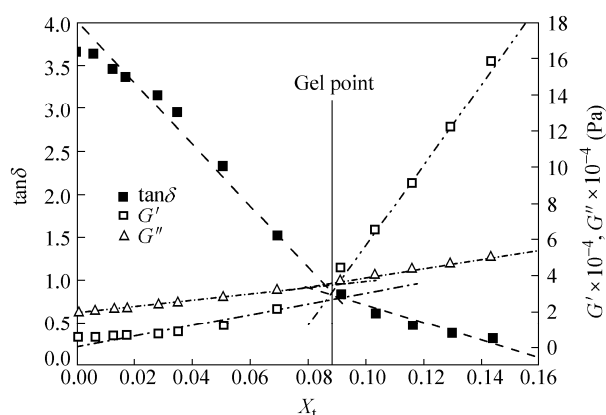


Fig. 10 Viscoelastic properties as a function of crystallinity during the isothermal crystallization process of PBS at 90°C ($\omega = 10$ rad/s)

CONCLUSIONS

Rheological method is an effective tool for the gel point determination of biodegradable semi-crystalline polymer PBS during isothermal crystallization. The dynamic moduli (G' and G'') exhibit the same growth characteristics. The rheological response of the system varies from viscous-dominated ($G' < G''$) to elastic-dominated ($G' > G''$), indicating the transition of liquid to solid. The frequency independence of the loss angle is used to determine the gel point. The results show that the gel time t_c and the gel strength S_g increase with the crystallization temperature, while the relaxation decreases, which is not in accordance with the results of *i*PP reported previously because the radial growth rate (the fibrous crystal growth rate for interconnected network formation) is faster than the inside crystallization rate (crystal growth rate for volume-filled) at high crystallization temperatures for PBS. The crystallinity at the gel point is very low (2.5%–8.5%), suggesting that the transition of liquid-to-solid in crystalline poly(butylene succinate) occurs at the very earliest stages of the crystallization process and only a few junctions are necessary to form a network spanning the entire sample. The network in this case must be “loosely” connected, meaning the critical gel is soft. The variation of G' , G'' , and $\tan\delta$ with crystallinity exhibits a sudden jump at the gel point.

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