Nanocellular Foaming Behaviors of Chain-Extended Poly(lactic acid) Induced by Isothermal Crystallization

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ABSTRACT: Recently, the fabrication of semicrystalline polymer foams with a nanocellular structure by supercritical fluids has been becoming a newly developing research hotspot, owing to their peculiar properties and prospective applications. In this work, a facile and effective isothermal crystallization-induced method was proposed to prepare nanocellular semicrystalline poly(lactic acid) (PLA) foams using CO2 as a physical blowing agent. Styrene−acrylonitrile−glycidyl methacrylate (SAG) as a chain extender (CE) was introduced into PLA through a melt-mixing method to improve the crystallization behavior and melt viscoelasticity of PLA. The chain extension reaction between PLA and SAG occurred successfully as well as the branching and micro cross-linking structures were generated in chain-extended PLA (CPLA) samples, which were confirmed by Fourier transform infrared spectra, gel fraction, and intrinsic viscosity measurements. Owing to the nucleation effect of branching points and the restricted movement of PLA molecular chains by the formation of branching and/or microcross-linking structures, a large number of small spherocrystals were generated in CPLA samples, which was beneficial to produce nanocells. Nanocellular CPLA foams were prepared successfully, when the foaming temperature was 125 °C. As the SAG content increased, the cell size of various PLA foams decreased from 364 ± 198 to 249 ± 100 nm and their volume expansion ratio increased from 1.15 ± 0.05 to 2.22 ± 0.01 times, gradually. When the foaming temperature increased from 125 to 127 °C, an interesting transition from nanocells to microcells could be observed in CPLA foam with the CE content of 2 wt %. Finally, the formation mechanism of nanocells in various PLA foams was proposed and clarified using a schematic diagram.

1. INTRODUCTION

In recent years, nanocellular polymer foams had aroused great interest in the scientific community because of their unique properties and promising applications.† Nanocellular polymer foams are generally defined as having the cell size less than 1 micron and the cell density greater than 1012 cells/cm³.‡,§ As a kind of newly developed material, nanocellular polymer foams possessed ultralow thermal conductivity and high toughness because of the Knudsen effect and the small cell size in the nanoscale, respectively.¶–‡ The nanocellular foams were found to be used in the fields of insulating materials, separation membranes, catalytic or dielectric applications, and so on.‖

The preparation method of nanocellular polymer foams included: phase separation method,⁺ sol–gel techniques,⁺⁺ molecular imprinting,⁺⁺⁺ batch-foaming method in an autoclave,⁺ extrusion-foaming method,⁺ injection molding,⁺⁺ and so on. In the methods stated above, the batch-foaming method in the autoclave by supercritical fluids had been proven to be a flexible and controllable method for the manufacture of nanocellular polymer foams.⁺⁺⁺ Currently, five kinds of polymers could be employed to prepare nanocellular foam: amorphous polymer,⁺⁺⁺ acrylic copolymer,⁺⁺⁺⁺ block copolymer with a high CO2-philic nanosized dispersed phase segments,⁺⁺⁺⁺⁺ polymer blend-containing nano-templates,⁺⁺⁺⁺ and polymer composites.⁺⁺⁺⁺ Amorphous polymers with an extremely large viscoelasticity could significantly restrict cell growth and coalescence. Nanocellular foams with cell sizes between 100 and 300 nm as well as relative densities between 0.15 and 0.3 were produced using acrylic copolymers and silica nanoparticles.⁺⁺⁺⁺ Low-density
nanocellular poly(methyl methacrylate) foam with an average cell size of 2.35 nm has been prepared at a very extremely low saturation temperature of −30 °C.

As a renewable resource-based aliphatic semicrystalline polyester, poly(lactic acid) (PLA) could be biodegraded and composted under favorable conditions. Compared with common PLA foams, nanocellular PLA foams could provide excellent properties for high value-added applications in the fields of membranes, sensors, and insulation materials. However, three big problems still existed in the fabrication of nanocellular PLA foams. First, the melt strength of PLA was low and its foamability was poor, which would promote the cell growth and mergence, leading to the formation of large cells. Second, the presence of the crystalline region (big spherocrystals) may impede the solubility and diffusion of blowing agent, which may further affect the cell nucleation and growth of PLA. Third, the cell nucleation point number in PLA melt without other foreign fillers, and/or the second phase was not adequate to meet the requirement of nanocellular polymer foams.

In order to solve the aforementioned problems, a rapid cooling foaming method was employed to prepare nanocellular chain-extended PLA (CPLA) foams in an autoclave by supercritical nitrogen, in which their average cell size could reach 600 nm. A similar rapid cooling foaming method was employed to produce nanocellular PLA bead foams with a double crystal-melting peak structure with supercritical CO2 in the autoclave. The volume expansion ratio (VER) of PLA bead foams could reach 30-fold and their average cell sizes ranged from 350 nm to 15 μm. In our previous study, a methodology of polymer blending and rapid cooling foaming was used to generate a complex cellular structure with large cells in microsize and small cells in nanosize in semicrystalline PLA foams, in which the small cell size could reach 396 nm.

Herein, we proposed a simple, facile, economical, environmentally friendly, and supercritical CO2 foaming-based method to prepare PLA nanocellular foams induced by isothermal crystallization. In this research, styrene–acrylonitrile–glycidyl methacrylate (SAG) as the chain extender (CE) was introduced into the PLA matrix to provide two obvious advantages. One was that the melt viscoelasticity of PLA may be improved to restrict cell growth and mergence. The other was that the spherocrystal size and number of PLA may be changed to increase cell density. The thermal properties, rheological properties, and foaming performance of various PLA samples were researched in detail. Moreover, the effect of SAG contents and foaming temperature on the cellular structural evolution of various PLA foams was also studied. This study was anticipated to give a useful method for preparing the nanocells in other semicrystalline polymers.

2. RESULTS AND DISCUSSION

2.1. Torque Curves. The chemical reaction between PLA and SAG could be qualitatively analyzed by changes in the torque values of various PLA samples. In Figure 1, a big peak could be observed in each curve of various PLA samples because of the addition of PLA and/or SAG. As the melting time increased, the torque curve of pure PLA decreased gradually, which should be resulted from the chain scission induced by thermal degradation and hydrolyzation. Interestingly, the torque curve of PLA–SAG increased with the melting time, indicating that the ring-opening reaction occurred between PLA and SAG. In order to observe the final torque values of various PLA samples clearly, their torque curves in 600–900 s were enlarged and placed in the upper left corner of Figure 1. It could be found that as the content of SAG increased, the final torque values of various PLA samples rose gradually, which would be attributed to the occurrence of chain extension as well as the formation of branching and cross-linking structures. Similar phenomenon was observed in our previous works. Based on the results of the torque curve, it could be speculated that the viscosity of PLA–SAG samples was enhanced with the increasing concentration of SAG.

2.2. Fourier Transform Infrared Spectra Analysis. The Fourier transform infrared spectroscopy (FTIR) spectra of various PLA samples and SAG are represented in Figure 2. In Figure 2a, several characteristic peaks of PLA could be seen in the FTIR spectra of various PLA samples, which were the C=O stretching vibration peak at 1751 cm⁻¹, the C–O vibration peak at 1183 cm⁻¹, the C–H deformation vibration peak at 1452 cm⁻¹, and the methyl characteristic peak at 1361 cm⁻¹, respectively. In Figure 2b, an obvious peak at 912 cm⁻¹ assigning to the stretching vibration of the epoxy ring could be seen in the FTIR spectrum of SAG. After the melt-mixing process of PLA and SAG, the peak of the epoxy ring at 912 cm⁻¹ disappeared in the spectra of PLA–SAG samples and the characteristic peak at 712 cm⁻¹ associating with the bending vibration of C–H out-of-plane of the benzene ring in SAG appeared in the PLA–SAG samples (in Figure 2c), indicating the occurrence of chain extension reaction between PLA and SAG.

2.3. Gel Fraction. Gel fraction was usually used to characterize the cross-linking degree of polymers. Considered on the chemical reaction between PLA and SAG, the gel fraction of various PLA samples is measured and summarized in Table 1. It could be seen from Table 1 that the gel fraction of various PLA samples increased gradually with the increment in SAG contents, which would be helpful to improve the viscoelasticity of PLA. The generation of gel indicated the occurrence of cross-linking reaction between PLA and SAG.
2.4. Crystallization and Melting Behaviors. The differential scanning calorimetry (DSC) curves of various PLA samples at the cooling (a) and heating (b) rates of 10 °C/min are shown in Figure 3. The isothermal crystallization curves of various PLA samples are shown in Figure 4a. The Avrami method was used to analyze the crystallization kinetic, and the double-ln plots of isothermal crystallization are displayed in Figure 4b. The corresponding thermal performance parameters obtained from DSC curves, including glass transition temperature \( T_g \), cold crystallization temperature \( T_{cc} \), melting temperature \( T_m \), crystallization kinetic constant \( k \), half time \( t_{1/2} \), crystallinity \( \chi_c \), are summarized in Table 2.

As shown in Table 2, with the increasing content of SAG, the \( T_g \) of various PLA samples was unchanged nearly, indicating that the length of the chain segment in various PLA samples changed hardly after chain extension. However, with the increment in the SAG content, the \( T_{cc} \) of various PLA samples increased and their \( T_m \) decreased, slightly and respectively. The increment in the \( T_{cc} \) of various PLA samples was probably because the formation of the branching structure in PLA−SAG samples restricted the movement of PLA molecular chains. The reduction in the \( T_m \) of various PLA samples should be ascribed to the decreasing perfection degree of the crystalline region in PLA by the formation of branching and/or cross-linking structures. Compared with that of pure PLA, the \( \chi_c \) of PLA−SAG samples increased slightly, which...
may be due to two aspects. On one hand, the branching points could be acted as the heterogeneous nucleation sites for PLA crystallization. On the other hand, the movement of molecular chains of PLA−SAG sample into the crystal lattice was restricted by the existence of branching and/or cross-linking structures. Based on the two following considerations, the foaming temperature was selected between \( T_{cc} \) and \( T_{m} \) in this research. One was that the high melt strength and viscosity of various PLA samples could be obtained because of the microcrystalline region acting the microcross-linking sites, which could be helpful for restricting the cell coalescence and growth. The other was that numerous interfaces between the crystalline region and amorphous region could be acted as the heterogeneous nucleation sites for cell nucleation, which were beneficial to increase cell density.

In addition, the \( k \) value and \( t_{1/2} \) of various PLA samples isothermally crystallized at 120 °C were measured to evaluate the crystallization rate and are shown in Table 2. Because the crystallization peak could not be observed clearly in the isothermal DSC trace of pure PLA as shown in Figure 4a, the \( k \) value and \( t_{1/2} \) of the pure PLA sample could not be calculated in this work. With the increasing SAG content, the \( k \) value of various PLA−SAG samples increased remarkably from \( 3.7 \times 10^{-5} \) to \( 1.4 \times 10^{-3} \). In addition, the \( t_{1/2} \) of the crystallization peak in DSC curves of various PLA−SAG samples decreased largely from 36.9 ± 0.5 to 19.8 ± 0.5 min, with the increment in the SAG content. This indicated that the crystallization rate of PLA was enhanced by the chain extension, which may be because the generated branching structure in CPLA could be acted as the crystallization nucleation point, resulting in the increment in the spherocrystal number (see Figure 5) and promoting the crystallization rate.

2.5. Polarized Optical Microscope Observation. In order to further study the effect of SAG contents on the crystal morphology of PLA, polarized optical microscopy (POM) was used to study the number and size of spherocrystals in various PLA−SAG samples isothermally crystallized for 40 min at 120 °C.
PLA samples. The crystal morphology of pure PLA is displayed in Figure 5a, in which a small amount of large spherocrystals was observed. The clear interface between the crystalline region and amorphous region indicated that the crystallization of pure PLA was a typical homogeneous nucleation. The crystal morphology of CPLA (PLA−SAG) samples is shown in Figure 5b−e. The spherocrystal number of various PLA−SAG samples increased with the increasing content of SAG. This should be attributed to the formation of branching structures which could be acted as the points of crystallization nucleation to enhance the number of spherocrystals after chain extension. The spherocrystal size of various PLA−SAG samples decreased as the content of SAG increased. The phenomenon could be explained by that the mobility of PLA molecular chains was reduced by the formation of branching and/or cross-linking structures. In summary, the generation of branching structure had double effects on the crystallization of PLA. The formation of branching structures in PLA−SAG samples was favorable for crystallization nucleation and disadvantageous for crystallization growth, resulting in the generation of a large number of small spherocrystals in PLA−SAG samples.

2.6. Intrinsic Viscosity ([η]) Measurements. In general, the [η] provided a measurement for the ability of an isolated and Gaussian polymer single chain to increase the viscosity of the solvent lacking of intermolecular interactions between polymer molecules. The inherent viscosity (η_inher) of each PLA sample at different solution concentrations is shown in Figure 6. There was a close relationship between the η_inher of polymer and the solution concentration. The [η] of polymer could be determined by extrapolating the concentration of polymer solution to zero. It could be seen in Table 3 that the [η] of various PLA samples increased with the increasing content of SAG, which should be attributed to the formation of branching and/or cross-linking structures. The branching degree of various PLA samples is shown in Table 4. The branching degree of various PLA samples increased with the increasing content of SAG, indicating the formation and increment of branching and/or microcross-linking structures.

2.7. Rheological Properties. The viscoelastic properties of polymer melt were generally tested by a dynamic rotational rheometer. The complex viscosity (η*), storage modules (G’), and loss factor (tan δ) of various PLA samples at different angular frequencies (ω) are shown in Figure 7. The η* of various PLA samples at different ω is displayed in Figure 7a. A typical behavior of pseudoplastic fluid was observed that was the shear thinning behaviors in the η* curves of various PLA samples. At low ω, the η* of various PLA samples increased with the increasing content of SAG, which should be attributed to the formation of branching and/or cross-linking structures. The branching structures would help to increase the melt viscosity of PLA as well as avoid cell mergence and rupture in the cell growth stage.
Figure 7b showed the $G'$ of various PLA samples at different $\omega$. The $G''$ of various PLA samples at low $\omega$ enhanced as the content of SAG increased, indicating that the melt elasticity of PLA was improved. In addition, with the SAG content increasing, the slope of all the $G''$ curves decreased. This phenomenon should be attributed to the formation of the branching and/or microcross-linking structures after chain extension. The increment in the melt elasticity was conducive to improve the foamability of PLA–SAG samples.

The tan $\delta$ of various PLA samples at different $\omega$ is shown in Figure 7c. The tan $\delta$ was defined as a ratio of loss modulus and $G''$ (i.e., viscous to elastic contribution) at a given $\omega$. It could be observed in Figure 6c that a big peak of mechanical loss appeared in the tan $\delta$ curve of pure PLA and PLA–SAG1 at the $\omega$ of 1 and 0.1 rad/s, respectively. The tan $\delta$ of PLA–SAG2, PLA–SAG3, and PLA–SAG4 decreased gradually with the increasing $\omega$. This indicated that their mechanical loss peak corresponding to the $\omega$ should be lower than 0.1 rad/s. With the increasing content of SAG, the tan $\delta$ of various PLA samples decreased gradually at the entire measured $\omega$ range, indicating that the elastic response of various PLA samples became fast, their viscous dissipation decreased gradually, and thus their foamability was enhanced. This phenomenon should be ascribed to the increment in the number of entanglement points in PLA–SAG samples after chain extension. Those entanglement points could be acted as the physical network sites to enhance the melt elasticity of PLA–SAG samples.

**2.8. Cellular Morphology.** Figures 8 and 9 show the cellular morphology and cell size distribution of various PLA foams prepared at 125 °C, respectively. Table 4 displays the foaming parameters of various PLA foams such as the cell size, cell density, and VER. It could be observed in Figure 7a that...
the cell walls of pure PLA were ruptured, and its cellular structure was incomplete, thus it was difficult to measure cell size and cell density. This phenomenon should be because the low melt strength of pure PLA was insufficient to support the cell growth, resulting in cell mergence and rupture. The cellular morphology of PLA foams became better after the chain extension because of the improved melt strength of PLA−SAG samples by the generation of branching and microcross-linking structures.

With the content of SAG increasing from 1 to 4 wt %, the cell size of various PLA−SAG foams gradually decreased from 364 ± 198 to 249 ± 100 nm, in which the cell size of PLA−SAG4 foam was much smaller than that of the PLA foams prepared in our previous studies. The reduction in the cell size of various PLA−SAG foams should be resulted from two aspects. On one hand, the crystalline region could not be biaxially stretched during the foaming process, which limited the cell growth to a certain extent. On the other hand, the entanglements formed by branching and micro cross-linking structures could be served as the cross-linking points to enhance the melt viscosity of PLA and limit cell growth. The cell size distribution of various PLA−SAG foams is shown in Figure 9. As the SAG content increased from 1 to 4 wt %, the cell size distribution of various PLA−SAG foams became narrow first and then kept unchanged. The cell density of various PLA foams increased first and then decreased slightly with the increasing content of SAG. The increment in cell density should be originated from two reasons. One was that the interface area between the crystalline region and amorphous region increased because of the formation of a large number of small spherocrystals (see Figure 5), which could be acted as heterogeneous cell nucleation points to increase cell density effectively. The other was that the improved melt elasticity of PLA−SAG samples (see Figure 7b) reduced the cell mergence, helping to increase cell density. With the SAG content increasing from 3 to 4 wt %, the slight decrement in the cell density of PLA−SAG foams should be attributed to the generation of a large amount of gel (see Table 1), restricting the cell nucleation and growth. The unfoamed regions in PLA−SAG4 foam are marked by yellow arrows in Figure 8e. The VER of various PLA foams increased gradually with the increasing content of SAG because of the increment in the G'' of various PLA samples (see Figure 7b).

Figures 10 and 11 show the cellular morphology and cell size distribution of PLA−SAG2 foams at different temperatures. Table 5 summarized the foaming parameters of PLA−SAG2 foams prepared at different temperatures, such as the cell size, cell density, and VER. As the foaming temperature increased, the cell size and VER of PLA−SAG2 foams increased as well as their cell density enhanced, gradually and remarkably. This phenomenon should be attributed to the decreased melt viscosity promoting the cell growth and mergence with the foaming temperature increasing. When the foaming temperature increased from 125 to 127 °C, an interesting transition from nanocells to microcells could be observed in PLA−SAG2 foams. Compared with the SAG content, foaming temperature had a significant influence on the cellular morphology evolution of various PLA foams.

2.9. Thermal Conductivity. The thermal conductivity of various PLA samples and their foams is shown in Table 6. The thermal conductivity of pure PLA sample and its foam was 1.77 ± 0.005 and 1.27 ± 0.006 W/(m·K), respectively. The decrement in the thermal conductivity indicated that the thermal insulation performance of pure PLA was greatly
improved after foaming because of the introduction of the cells and the lower thermal conductivity of air. It could be seen from the thermal conductivity of various PLA samples that chain extension had little effect on the thermal conductivity of the unfoamed PLA samples but large effect on the thermal conductivity of PLA foams due to the variation of foaming properties. With the SAG content increasing from 0 to 4 wt %, the thermal conductivity of various PLA foams decreased from $0.127 \pm 0.006$ to $0.080 \pm 0.005$ W/(m·K). This implied that the thermal insulation property of PLA foams was improved after chain extension, which should be attributed to the decrement in the cell size to the nanoscale (probably generating Knudsen effect). Besides this, the decrement in the thermal conductivity of various PLA foams looked to have a relationship with the reduction in foam density.49,50

2.10. Foaming Mechanism. In general, the formation of nanocells in the polymer foams depended on two aspects. One was the sufficient cell nucleation sites to promote cell nucleation, resulting in the high cell density. The other was the favorable melt viscoelasticity to restrict the cell growth and avoid the cell mergence, leading to the expected small cell size.

In this work, an isothermal crystallization-induced method was proposed to produce numerous and small spherocrystals in various PLA samples, which were helpful for generating nanocells. As displayed in Figure 12, with the SAG content increasing, the molecular chain architecture of various PLA samples would change from linear to branching and/or cross-linking structures (see Tables 1 and 3). Because of the nucleation effect of branching points and the restricted movement of PLA molecular chains by the formation of branching and/or cross-linking structures, the spherocrystal number of various PLA samples increased and their size decreased, indicating that the interface area between the crystalline region and amorphous region enhanced. Because the interface between the crystalline region and amorphous region could be acted as the cell nucleation sites2,48 the cell density of various PLA foams was promoted significantly. Besides this, the formed numerous and small spherocrystals would decrease the solubility and diffusion of CO$_2$ in PLA matrix and could be served as physical cross-linking sites to

![Figure 10. Cellular morphology of PLA–SAG2 foams at various foaming temperatures: (a) 123, (b) 125, (c) 127, (d) 129 °C.](image)

![Figure 11. Cell size distribution of PLA–SAG2 foams at various foaming temperatures: (a) 125, (b) 127, (c) 129 °C.](image)
enhance the melt viscoelasticity. Both the two aspects would limit the cell growth and mergence, which were beneficial to generate the cell size in nanometer and increase the cell density significantly.

3. CONCLUSIONS

In this paper, nanocellular PLA foams were fabricated successfully by an isothermal crystallization induction method in the presence of supercritical CO2. The crystallization behaviors and rheological properties of various PLA samples were improved by the chain extension reaction using SAG as CE. The results of gel content and $[\eta]$ showed that the branching and micro cross-linking structures were generated in PLA–SAG samples. POM images displayed that the spherocrystal number of various PLA samples increased and their size decreased, with the increasing content of SAG. As the content of SAG increased from 1 to 4 wt %, the cell size of various PLA foams decreased gradually and the smallest cell size could reach 249 ± 100 nm. With the foaming temperature increasing from 125 to 127 °C, an interesting transition from nanocells to microcells was observed in PLA–SAG2 foams. The chain extension was positive to enhance the thermal insulation performance of various PLA foams by decreasing their foam density. This study may provide a feasible method for the fabrication of nanocells in other semicrystalline polymers.

4. EXPERIMENTAL SECTION

4.1. Materials. PLA (2003 D) was purchased from Nature Works Inc. It has the melt flow rate of 3.2 g/10 min (190 °C, 2.16 kg), the D-isomer content of approximately 4.3%, the density of 1.24 g/cm3, the glass transition and melting temperature of 61.4 and 147.6 °C, respectively. SAG (its product grade: SAG-008) is a random SAG terpolymer with the epoxy content of 8 ± 0.5 wt %, which was supplied by Fine-Blend Compatibilizer Jiangsu Co., China.

4.2. Preparation of Various PLA Samples. Prior to melt blending, PLA and SAG were dried in a vacuum oven at 80 °C for 6 h to remove moisture and eliminate the influence of moisture on the experiment. The melting temperature, mixing time, and mixing speed were 180 °C, 15 min, and 80 rpm, respectively. According to the formula shown in Table 7, PLA and SAG with various blending ratios were fed into a Haake internal mixer. The corresponding sample names were denoted as pure PLA, PLA–SAG1, PLA–SAG2, PLA–SAG3, and PLA–SAG4, respectively. Subsequently, the resultant samples were placed and pressed in a mold at 190 °C and 10 MPa for 10 min and then cooled to room temperature to form sheet samples with the thickness of 1 mm. According to the preparation method mentioned above, at least five samples in each category of various PLA samples were produced. Finally, the small sheet with 1 cm × 1 cm (length × width) was cut in the center of each sample for further characterization and foaming process.

4.3. Foaming Process of Various PLA Samples. Various PLA samples were foamed in a stainless-steel autoclave using supercritical CO2 as a physical foaming agent. The schematic

![Figure 12. Possible formation schematic of nanocells in various PLA foams.](https://example.com/figure12.png)
The diagram of the autoclave for batch foaming was introduced in detail in our previous study. First, the PLA samples were placed into an autoclave for 2 h at the saturation pressure of 10 MPa and the constant foaming temperature of 123, 125, 127, and 129 °C, respectively. After the CO₂ was completely diffused and dissolved in the PLA matrix, the pressure of the autoclave was dropped by releasing CO₂ from 10 to 0.1 MPa in about 6 s, providing a driving force for cell nucleation and growth to produce various PLA foams.

4.4. Characterizations. 4.4.1. Fourier Transform Infrared Spectroscopy. The FTIR spectra of various PLA samples were measured at the room temperature using a Nicolet IZ10 spectrometer. Various PLA samples were placed on the sample stand and measured with 32 scans at a resolution of 2 cm⁻¹. Each spectrum was recorded within the range of 3500–500 cm⁻¹.

4.4.2. Gel Fraction Measurement. The gel fraction of various PLA samples was tested by Soxhlet extraction with chloroform until the weight did not vary anymore. Then, various PLA samples were dried in an oven for 6 h at 80 °C. The gel fraction of various PLA samples could be calculated by eq 1:

$$\text{Gel fraction} = \frac{w_0}{w_g} \times 100\%$$  \hspace{1cm} (1)

in which, $w_0$ and $w_g$ are the original weight of various PLA samples and the weight of dried insoluble part in various PLA samples, respectively.

4.4.3. Differential Scanning Calorimetry. The crystallization and melting behaviors of various PLA samples were studied by DSC (Q20, TA, USA). Approximated 5–10 mg of each PLA sample was quickly heated to 190 °C, held for 5 min to eliminate the heat history, and then decreased to 40 °C by the cooling rate of 10 °C/min, finally reheated to 190 °C by the heating rate of 10 °C/min. The $X_c$ of various PLA samples was computed by eq 2.

$$X_c(\text{PLA}) = \frac{\Delta H_m(\text{PLA}) - \Delta H_c(\text{PLA})}{\Delta H_m(\text{PLA})} \times 100\%$$  \hspace{1cm} (2)

In which, $\Delta H_m(\text{PLA})$ is the melting enthalpy of PLA, $\Delta H_c(\text{PLA})$ is the cold crystallization enthalpy of PLA, and $\Delta H_m(\text{PLA})$ is the melting enthalpy of 100% crystalline PLA that is 93 J/g.54

In order to evaluate the crystallization rate of various PLA samples, PLA samples were heated from room temperature to 200 °C at the rate of 30 °C/min, held for 5 min to eliminate thermal history, then cooled down 120 °C at the rate of 30 °C/min, and kept for 40 min to observe their crystal morphology changes. 4.4.4. [$\eta$]. The [$\eta$] of various PLA samples was measured by an Ubbelohde viscometer. To keep the temperature constant in the entire test, the viscometer was immersed in a thermostatic water bath at 25 °C. Each PLA sample was dissolved in chloroform, forming five different concentrations and placed into a volumetric flask of 25 mL. The flowing time measurements for each concentration were repeated five times and then averaged to ensure the result accuracy. Finally, the [$\eta$] and branching degree of various PLA samples were calculated by the equations reported in the literature.

4.4.6. Rheological Properties. The dynamic rheological properties of various PLA samples were tested using a rotational rheometer (ARES Rheometer, TA, USA) at 190 °C with a pair of parallel plates (20 mm in diameter with a gap of 1.0 mm). The frequency range was 0.1–100 rad/s, and the maximum strain was fixed at 5% to make sure that these conditions were within the linear viscoelastic region under nitrogen. The $\eta^*$, storage modules $G'$, and tan $\delta$ were measured at various angular frequencies.

4.4.7. Scanning Electron Microscope. The cellular morphology of various PLA foams was observed by scanning electron microscopy (SEM) at an accelerating voltage of 5 kV. Each PLA foam was immersed in liquid nitrogen for 4 h and then fractured quickly in air. Prior to observation, the fracture surfaces of various PLA foams were sputter-coated with Au to prevent accumulation of static charge during observation.

4.4.8. Foaming Properties. The VER ($\phi$) of various PLA foams was calculated by eq 3:

$$\phi = \frac{\rho_p}{\rho_f}$$

where $\rho_p$ and $\rho_f$ are the bulk densities of the prefoam and postfoam samples in g/cm³, respectively, which were measured by a density balance (Sartorius, Goettingen, Germany).

Cell density ($N_0$) (cells/cm³) was analyzed using the software image tool and calculated by eq 4:

$$N_0 = \left[ \frac{nM^2}{A} \right]^{1/2} \phi$$

where $n$ is the number of cells in the SEM micrograph, $M$ is the magnification factor, and $A$ is the area of the micrograph (in cm²).

4.4.9. Thermal Insulation Performance. A laser thermal conductivity analyzer (LFA467, NETZSCH Scientific Instruments Co., Ltd, GER) was used to measure the thermal conductivity of various PLA samples and their foams at 25 °C. The prepared samples with the thickness of 1 mm were cut into the small sheet with 10 mm × 10 mm (length × width) as well as their surface was kept parallel. Each sample was measured five times, and the average value was recorded.

Table 7. Formula of Various PLA Samples

| sample name | pure PLA | PLA–SAG1 | PLA–SAG2 | PLA–SAG3 | PLA–SAG4 |
|-------------|----------|----------|----------|----------|----------|
| PLA (wt %)  | 100      | 99       | 98       | 97       | 96       |
| SAG (wt %)  | 0        | 1        | 2        | 3        | 4        |

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