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## Cell nucleation in dominating formation of bimodal cell structure in polypropylene/polystyrene blend foams prepared via continuous extrusion with supercritical CO<sub>2</sub> (Post-print)

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### Abstract

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### Full Text

### Preamble

#### Cell Nucleation in Dominating Formation of Bimodal Cell Structure in Polypropylene/Polystyrene Blend Foams Prepared via Continuous Extrusion with Supercritical CO

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**Keywords:** Bimodal cell structure; Supercritical CO<sub>2</sub>; Continuous extrusion foaming; PP/PS blend; Cell nucleation

**Abstract:** It is generally difficult to predict the cell structure foamed from a binary polymer blend compared to a single polymer, as many factors in polymer blends add to the complexity of the foaming process without easy control, such as blend morphology, blend viscosity, and solubility and diffusivity of the

foaming agent, etc. In this study, polypropylene (PP)/polystyrene (PS) blend foams with a bimodal cell structure were prepared by using supercritical carbon dioxide (scCO<sub>2</sub>) in continuous extrusion. By comparison of the cell structure of blend foams before and after extraction, it was found that the large cells were mainly formed in PS phase, while the small ones were mostly formed in PP phase. A possible mechanism was proposed to explain the formation of the bimodal cell structure. It was believed that a prominent difference in cell nucleation in the two phases of the PP/PS blends was required for the formation of bimodal cell structure. The proposed mechanism was confirmed by further experimental results, which showed that the bimodal cell structure could be changed by altering the nucleation ability in PP phase and PS phase through changing experimental conditions, such as the content of scCO<sub>2</sub> and the pressure drop, or through applying a heterogeneous nucleating agent.

## 1. Introduction

Polymer foams are widely-used materials prepared with a distinct cellular structure via the expansion of a blowing agent. These foams are widely used in various applications from packaging, insulation, transportation and construction [1-6]. Among them, the foams with distinctive bimodal cell structure have proved to possess excellent properties, such as thermal insulation and mechanical performance [7,8]. Consequently, generating cellular structure with large and small cells has attracted great attention from both academic and industrial points of view.

A number of studies have been reported on how to create foams with a bimodal cell structure [7-11]. The most commonly applied approach is to use a two-step depressurization batch foaming technology, through which the bimodal foams can be obtained by depressurization in two distinct steps [9,10]. Arora et al. [9] reported that PS foams with a bimodal cell structure were produced through two-stage depressurization in a batch foaming process. The results showed that the large cells and the small ones were formed in the first and the second depressurization stage, respectively, and that the small ones were nucleated and grown within the cell walls of the formed large ones. However, this approach cannot be carried out in a continuous extrusion foaming process. Another method involves application of two different blowing agents to induce two foaming characteristics [7,8,11]. Lee et al. [7] prepared bimodal PS foams blown with n-butane and water in extrusion. They reported that the formation of the small cells was attributed to the trapped water in the pore of silica (water carrier), while that of the large ones was mainly resulted from the excessive water and n-butane. However, use of a second blowing agent involves a more complex process, and some blowing agents (e.g. n-butane) were inflammable.

As mentioned above, the bimodal cell structure has been successfully obtained in a single polymer. However, it is not easy to prepare bimodal cell structures in polymer blend foams due to the different foaming characteristics and mechanisms of different components. When foams are prepared from polymer

blends, the cell structure is affected by many factors, such as the viscosity of the polymers, the phase morphology, the interfacial areas, and the solubility and diffusivity of the blowing agent in different polymer components, etc. [12]. Some studies have reported that various cell structures were obtained through foaming from polymer blends [12-15]. Doroudiani et al. [13] reported that the cell morphology of polypropylene (PP)/high-density polyethylene (HDPE) blend foams was much finer and more uniform than that of neat HDPE and PP, although the blend foams showed no bimodal cell structure. By applying a one-step batch foaming process, Taki et al. [12] fabricated PS/poly(ethylene glycol) (PEG) blend foams with a unique bimodal cellular structure, which were mostly attributed to the mass transfer of CO<sub>2</sub> and the viscosity change of the blends.

It is well accepted that PP/PS blend is a useful polymer blend system, which is among the most widely used plastics due to the excellent properties of PP and PS. It is of great significance to investigate the foaming behavior of PP/PS blends for industrialization purpose. As previously reported [16-18], the cell structures of pure PP and PS foams are completely different due to their different physical properties. Therefore, it is highly expected that the cell structures of the PP/PS blend foams would be dependent on the properties and the content of each component. For example, Huang et al. [18] prepared microcellular PP/PS blend foams with tunable cell structure through a batch foaming process, and they found that the cell structure was strongly dependent on the blend phase morphology and the solubility of CO<sub>2</sub> in both PP phase and PS phase. However, no bimodal cell structure was formed in their study, probably due to that PP could hardly be well foamed via a batch foaming process. Up to now, no intensive work has been reported on preparation of PP/PS blend foams with bimodal cell structure through continuous extrusion foaming. Based on the previous literatures [19,20], the solubility of CO<sub>2</sub> in PP and PS melts are quite different, and hence, the cell nucleation would be different in the two phases. Thereby, it is highly expected that the bimodal cell structure could be formed in PP/PS blends during continuous extrusion foaming.

In this study, PP/PS blend foams with a bimodal cell structure were prepared in continuous extrusion foaming with scCO<sub>2</sub> as the foaming agent. The cell nucleation in terms of different affinities of PP phase and PS phase for scCO<sub>2</sub> was discussed on how to affect the formation of bimodal cell structure. A possible mechanism was proposed to explain the formation process of the bimodal cell structure. Various experimental conditions were applied via changing the content of scCO<sub>2</sub> or the pressure drop to verify the proposed mechanism. In addition, a heterogeneous nucleation agent was added into the PP/PS blends to further study the effect of alteration of the cell nucleation ability in PP and PS phases on formation of bimodal cell structure. As such, the cell nucleation has proved to be a significant factor in dominating the formation of bimodal cell structure in the binary polymer blends.

## 2.1. Materials

PP (grade PPB-M02) used in this study was a linear copolymer, provided by Sinopec Zhenhai Refining & Chemical Company (China). It has a MFI of 1.6 g/10 min at 230 °C/2.16 kg, a melting temperature of 167 °C and a crystallization temperature of 110 °C. PS (grade GPPS251) used was supplied by Shanghai Secco Petrochemical Co., Ltd. It has a MFI of 2.5 g/10 min at 200 °C/5 kg and a glass transition temperature of 95 °C. The clay (grade DK4) used was obtained from Zhejiang Fenghong New Material Co., Ltd. It has a particle size of 5-15 (cid:2)m, cation-exchange capacity of 90 meq/100 g and interlayer spacing of 1.3 nm. The physical blowing agent, CO (99% purity), was provided by Ningbo Wanli Gas Corporation.

Compositions of PP/PS blends and PP/PS/clay composites.

Sample	PP content (wt%)	PS content (wt%)	Clay content (wt%)
PP90/PS10	90	10	0
PP80/PS20	80	20	0
PP70/PS30	70	30	0
PP60/PS40	60	40	0
PP/clay	100	0	1
PP90/PS10/clay	90	10	1
PP80/PS20/clay	80	20	1
PP70/PS30/clay	70	30	1
PP60/PS40/clay	60	40	1
PS/clay	0	100	1

*PP and PS are polypropylene and polystyrene, respectively.*

## 2.2. Sample Preparation and Extrusion Foaming

PP, PS and clay were vacuum-dried at 60 °C for 8 h before use. PP/PS premix and PP/PS/clay premix were prepared by dry-blending in a bag. Subsequently, the premix was fed into a tandem single screw extruder for extrusion foaming. Compositions of the PP/PS blends and PP/PS/clay composites are shown in Table 1.

The tandem extrusion system used in this study is shown in [Figure 1: see original paper]. It consisted of two extruders, an ISCO syringe pump to inject CO into the polymer melts, a heat exchanger with homogenizing static mixers, a gear pump (Zenith, PEP-II) and a nozzle. The first extruder with a screw diameter of 45 mm was driven by a 25 hp drive motor (SIMO, Z4-132-3), and the second extruder with a screw diameter of 65 mm was driven by a 40 hp drive motor (SIMO, Z4-160-31). The first extruder was used to plasticize the polymer resin and to preliminarily mix the polymer and the gas, with a rotating speed and a processing temperature set at 36 rpm and 190 °C, respectively. The

second extruder was used to cool the polymer melt and to completely dissolve the gas in the polymer melt, with the processing temperature set at 180–160 °C. The temperature of the capillary die was set equivalent to that of the second extruder.

The content of CO<sub>2</sub> injected into the extruder was adjusted by controlling both the materials feed rate and the CO<sub>2</sub> flow rate through a syringe pump. The applied content of CO<sub>2</sub> was either lower than its solubility in both PS and PP, or higher than its solubility in PS while lower than that in PP, to make sure that the applied CO<sub>2</sub> could completely dissolve in the polymer melts. The CO<sub>2</sub> was injected into the polymer melts at the three-quarter section of the first extruder at a pressure of 18.0 MPa, which was much higher than the pressure of the polymer melts in the first extruder (about 7.0 MPa). The high injection pressure would promote scCO<sub>2</sub> to quickly diffuse into the polymer melts. In addition, based on the reported literature [21,22], a homogeneous polymer/gas solution could be formed in seconds during mixing due to the strong shearing from the screw and the static mixers. In this study, the mixing and residential time for scCO<sub>2</sub> in the extruders was about 15 min. Due to the high injection pressure, the strong shear from the screw and the static mixers as well as the strong diffusivity of scCO<sub>2</sub>, the mixing and residential time of 15 min was considered enough for scCO<sub>2</sub> to completely dissolve in the polymer melts to form a homogeneous polymer/gas solution. When the uniformly mixed polymer/scCO<sub>2</sub> solution finally passed through the die, the solubility of scCO<sub>2</sub> in the polymer would undergo a sudden decrease due to the fast pressure drop. Consequently, numbers of cells were nucleated and the foam structure was formed with the cells growing. The foamed samples were collected for observation of the cell morphologies and measurement of the foam density.

It is noted here that the processing pressure in the second extruder was maintained at 10.5–18.0 MPa, which was controlled by three different nozzles as listed in Table 2. Nozzle A was used for the lowest processing pressure and Nozzle C for the highest. Three different nozzles were used in section 3.4.2 to obtain different pressure drops, while in the rest of the study, only Nozzle A was applied.

### 2.3. Characterizations

Scanning electron microscope (SEM, Hitachi TM-1000) was used to observe the morphology of PP/PS blends and the cell morphology of the foamed samples. The samples were freeze-fractured in liquid nitrogen and sputter-coated with gold before observation.

The cross-section of some blend foams was dyed with a black marker pen, and then the cell structures of the treated foams were observed by a polarized optical microscopy (POM, Olympus H-601). After that, the treated foams were extracted by xylene at room temperature for 12 h and then were observed again by POM. In other words, the cell structures of the blend foams were observed

by the POM both before and after extraction.

The mass densities of the samples before ((cid:2)) and after ((cid:2)f) foaming were measured by the water displacement method based on ISO 1183-1987. Cell density and size were determined from the SEM micrographs. The cell diameter was the averaged size of at least 100 cells in the SEM micrograph. The cell density ( $N$ ), defined as the number of cells per cubic centimeter of unfoamed polymer, was determined based on Eq. (1) as follows:

$$N_0 = \left(\frac{n}{A}\right)^{3/2} \times \frac{(cid:3)}{(cid:3)_f}$$

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  $\text{cm}^2$ ). ((cid:3)) is the volume expansion ratio of the polymer foam, which can be calculated through Eq. (2):

$$(cid:3) = \frac{(cid:2)}{(cid:2)_f}$$

### 3.1. Phase Morphology of PP/PS Blends

The morphology of the PP/PS blends without and with extraction by xylene was studied by SEM, and the results are shown in [Figure 2: see original paper]. After extraction, the etched phase was the PS rich phase. From the two series of the samples without or with extraction, it could be clearly seen that sea-island morphology was formed for all the PP/PS blends, with PS as the dispersed phase and PP as the continuous phase. As the content of PS in the blends was increased, the dispersed phase was increased in size from around ((cid:2)m) to 4.0 ((cid:2)m). For PP60/PS40 blend, although the PS-rich phase still formed the dispersed phase, it already showed some tendency to coalesce for the blend to form co-continuous structure. The correlation between the foam structure and the phase morphology of the PP/PS blends will be discussed later.

### 3.2. Bimodal Cell Structure in PP/PS Blends

Cell structures of pure PP and pure PS foams prepared via extrusion foaming with 5.0 wt% scCO<sub>2</sub> at a foaming temperature of 165 °C are shown in [Figure 3: see original paper]a and b, respectively. It was found that pure PP foam had a smaller average cell size (200 ((cid:2)m)) and higher cell density ( $5.97 \times 10^8$  cells/ $\text{cm}^3$ ) than pure PS foam (350 ((cid:2)m)) and  $10^8$  cells/ $\text{cm}^3$ , respectively). As previously reported by Sato et al. [19,20], the solubility of CO<sub>2</sub> in PP and PS melts were 7.2-18.4 and 4.1-8.1 g/100 g in the temperature range of 160-175 °C and the pressure range of 10.5-18.0 MPa, respectively. Based on that, the solubility of CO<sub>2</sub> under the experimental condition (165 °C, 10.5 MPa) in this study was about 7.8 g/100 g in PP and about 4.6 g/100 g in PS. It indicated that the CO<sub>2</sub> had a higher solubility in PP melt than in PS melt, which could

lead to a higher cell nucleation ability in PP, and consequently, a higher cell density and a smaller average cell size [23].

The cell structures of PP/PS blend foams with 10, 20, 30, and 40 wt% PS are shown in [Figure 3: see original paper]c-f. For PP90/PS10 blend foam, the cell structure did not show significant changes relative to pure PP foam, due to the lower content and smaller average domain size of the dispersed PS phase. However, with an increase in PS content, a bimodal cell structure was observed in PP80/PS20 blend foam. The average size of large cells was around 400 (cid:2)m, slightly larger than the average cell size of pure PS foam. Whereas, the average size of small cells was around 80 (cid:2)m, much smaller than the average cell size of pure PP foam. Similar bimodal cell structure was also observed in PP70/PS30 and PP60/PS40 foams, and the number of large cells increased with the PS concentrations. Therefore, through comparing the cell size of PP/PS blend foams with that of pure PP and PS, it was speculated that the large cells were mostly formed in PS rich phase, while the small ones were mainly formed in PP rich phase.

In order to prove that from which phase the large cells and the small ones were formed, POM was applied to investigate the morphology change of the cross-section of the blend foams before and after extraction by xylene. It is known that PS dissolves in xylene at room temperature while PP doesn't. Therefore, if the cell walls of the large cells dissolved in xylene after etched instead of those of the small ones, it could prove that the large cells of the PP/PS blend foams were formed from the PS rich phase and the small ones were formed from the PP rich phase. The POM images of PP/PS blend foams at the same position before and after extraction by xylene are shown in [Figure 4: see original paper]. The large black areas in the images represented many neighboring small cells. Comparing the images in the lower row with the upper ones, it was found that some cell walls between the large cells were extracted by xylene, while almost all those between the small cells were unchanged. Hence, the results indicated that the large cells were mainly formed in PS rich phase, while the small ones were formed in PP rich phase.

### 3.3. Formation Mechanism of Bimodal Cell Structure in the Binary Polymer Blend

In order to better understand the formation process of the bimodal cell structure from the melt state of the binary polymer blend, a possible mechanism was proposed in [Figure 5: see original paper] based on the results discussed above. Figure 5: see original paper shows mixing and dispersion states of the PP/PS blend during the extrusion process with the dissolved scCO<sub>2</sub>. Once the polymers/gas solution was extruded from the die, the cells were preferentially nucleated in the PP rich phase and at the PP/PS interface (Figure 5: see original paper). During the extrusion foaming process, PP melt had a higher affinity for scCO<sub>2</sub> than PS [19,20], thus it resulted in an enhanced cell nucleation in PP phase [12]. Also, the cell nucleation was enhanced at the interphase regions due

to the reduced energy barrier, according to the classical heterogeneous nucleation theory [24].

The higher scCO solubility in PP melts than in PS induced a large scCO concentration gradient across the PP/PS interface. Once the pressure was released at the die, the system was destabilized and deviated from the equilibrium state. Due to the large scCO concentration gradient across the PP/PS interface, the diffusion of scCO was driven from the PP phase to the PS phase (Figure 5: see original paper) [18,23]. Consequently, the cell nucleation in the interfacial regions and in the PS phase would be largely enhanced. Besides the enhanced nucleation ability in PS phase, the excess scCO could also promote the growth of PS cells. Due to the persistent pressure difference between the PP phase and the PS phase, the large cells (in PS phase) became even larger, whereas the growth of small cells (in PP phase) was hindered (Figure 5: see original paper). Eventually, the transfer of scCO caused the average size of large cells in PP/PS blend foam larger than the average cell size of pure PS foam, while that of small ones much smaller than the average cell size of pure PP foam ([Figure 3: see original paper]). Once after the temperature was decreased below the crystallization temperature of PP, the bimodal cell structure was almost stabilized (Figure 5: see original paper). In summary, it was proposed that the difference of the cell nucleation in the two phases of the binary PP/PS blends played a key role in dominating the bimodal cell structure.

### 3.4. Alteration of Cell Nucleation in Changing Cell Structures

It was mentioned that the PP melt (solubility: 7.8 g/100 g) has a higher affinity for CO than PS (solubility: 4.6 g/100 g) did at the foaming temperature of 165 °C and scCO content of 5.0 wt%, so the number of the nuclei in the PP phase should be larger than those in the PS phase in PP/PS blends. Consequently, the cell density was much higher in the former one than in the later one, while the cell size was smaller for the former one. Thus, it was proposed that the difference of the nuclei density in two phases of a polymer blend played a significant role in dominating the bimodal cell structure. Further, it could be imagined that if the difference was big enough, the bimodal cell structure should be formed in a polymer blend foam. In comparison, if the difference was negligible, or if it was altered to be reduced by changing experimental conditions or by adding a heterogeneous cell nucleating agent, the bimodal cell structure would not be formed. In order to verify the proposed mechanism, the effect of various experimental conditions on the cell structures of PP70/PS30 blend as well as pure PP and pure PS was studied, and the results were discussed in the following paragraphs.

### 3.4.1. Effect of Content of scCO on Cell Structures

[Figure 6: see original paper] shows the effect of content of scCO on the cell structures of PP, PS and PP70/PS30 foams. It is noted here that the suitable foaming temperature for a polymer was decreased with increased contents of scCO, due to the enhanced plasticizing effect of scCO. In this study, the suitable foaming temperature was 175, 170, 165, 160 °C for the foams prepared with 1.0, 3.0, 5.0, 7.0 wt% scCO, respectively. All the system pressures in the second extruder were maintained at about 10.5 MPa using Nozzle A for preparation of foams with various contents of scCO. For the three foams shown in [Figure 6: see original paper], a small quantity of cells with thick cell walls were formed with 1.0 wt% scCO, while the number of cells was significantly increased with 3.0 wt% scCO. With further increase of scCO, the cell densities continued to increase and the cell walls turned even thinner. Moreover, both the pure PP and PS foams showed uniform cell structures at various contents of scCO. However, the PP70/PS30 foam showed uniform cell structures at low scCO contents (1.0 wt% and 3.0 wt%), while it showed bimodal cell structures with 5.0 wt% and 7.0 wt% scCO.

Concerning the formation of the bimodal cell structure in the binary polymer blend at higher contents of scCO instead of at lower contents, it was considered to depend on a prominent difference in nuclei density formed in different phases, which was affected and thus could be altered by changing the dissolved contents of scCO. To clarify this issue, it would be easier to interpret and thus to be understood via mathematically comparing the content of scCO applied in the continuous extrusion with its solubility in PP and PS in value. If the content of scCO injected in the continuous extrusion was lower than its solubility in PS at a given experimental condition, scCO could completely dissolve in both PP and PS phases, as the solubility of scCO in PS was lower than that in PP in the temperature range of 175–160 °C [19,20]. In this case, similar cell nuclei density might be formed in both phases, and then the cells would grow to similar sizes without formation of bimodal cell structure.

In comparison, if the content of scCO injected in the continuous extrusion was higher than its solubility in PS but lower than that in PP, then the dissolved content of scCO was higher in PP phase than in PS phase. Thus, a difference of the dissolved content of scCO existed between PP phase and PS phase, which could induce the difference of the cell nucleation in the two phases, resultantly forming the bimodal cell structure.

The conjecture could be confirmed by the cell densities of the PP, PS and PP70/PS30 foams prepared at different contents of scCO, which were calculated based on the SEM images and are shown in [Figure 7: see original paper]. With 1.0 wt% scCO, the processing temperature of continuous extrusion was 175 °C. Based on the literature [19,20], the solubility of CO in PS and PP at 175 °C was about 4.1 and 7.2 g/100 g, respectively. As the injected content of scCO was lower than its solubility in both phases, it would completely dissolve in both of

them, and thus the nuclei density was similar for the two phases in PP70/PS30. This could be supported by cell density data at 1.0 wt% scCO<sub>2</sub> in [Figure 7: see original paper], which shows that the cell density in PP, PS and PP70/PS30 foams was almost the same.

Similarly, with 3.0 wt% scCO<sub>2</sub> (corresponding to a processing temperature of 170 °C), the solubility of CO<sub>2</sub> in PS and PP was about 4.3 and 7.5 g/100 g, respectively [19,20]. Similar cell density was also formed for both phases, which was evidenced by the cell density data at 3.0 wt% scCO<sub>2</sub> in [Figure 7: see original paper]. Therefore, bimodal cell structure was not formed in PP70/PS30 foam prepared with 3.0 wt% scCO<sub>2</sub>.

In comparison, with 5.0 wt% scCO<sub>2</sub> (corresponding to a processing temperature of 165 °C), the solubility of CO<sub>2</sub> in PS and PP at 165 °C was about 4.6 and 7.8 g/100 g, respectively [19,20]. The higher content of dissolved CO<sub>2</sub> in PP phase than in PS phase in PP70/PS30 would result in a difference in cell nucleation and thus a bimodal cell structure. This was confirmed by the cell density data at 5.0 wt% scCO<sub>2</sub> in [Figure 7: see original paper], which shows a prominent difference in cell density in PP and PS. Similarly, with 7.0 wt% scCO<sub>2</sub> (corresponding to a processing temperature of 165 °C), the solubility of CO<sub>2</sub> in PS and PP was about 4.8 and 8.1 g/100 g, respectively [19,20]. The different cell nucleation density formed in PP and PS phases due to a larger dissolved content in the former one was supported by the cell density data in [Figure 7: see original paper], and consequently, bimodal cell structure was formed in PP70/PS30 foam prepared with 7.0 wt% scCO<sub>2</sub>. In summary, the cell density data in [Figure 7: see original paper] confirmed the conjecture we proposed that a prominent difference in cell nucleation density formed in different phases in the binary blend dominated the formation of bimodal cell structure, and that the cell nucleation could be affected and hence altered by changing the dissolved contents of scCO<sub>2</sub>.

### 3.4.2. Effect of Pressure Drop on Cell Structures

It is well known that for polymer foaming, cell nucleation is initiated by a thermodynamic instability of a polymer/gas solution. As the solubility of the gas in polymer melts decreases with the system pressure, thus, the thermodynamic instability could be induced by a rapid pressure drop along the nozzle. Therefore, the pressure drop plays a significant role in controlling cell nucleation ability during continuous extrusion foaming [25]. The pressure drop for a non-Newtonian fluid can be theoretically calculated by adopting a “power law” model [26]. In this section, three types of nozzles were applied to generate different pressure drop. The die geometries and the corresponding pressure drop are summarized in Table 2.

Specifications of nozzles used in this study.

Nozzle	Filament Diameter (mm)	Length (mm)	Pressure drop (MPa)
Nozzle A	1.0	10	10.5
Nozzle B	0.5	10	13.0
Nozzle C	0.5	5	18.0

It should be noted that the whole system pressure in the second extruder was maintained similar as that at the end of the nozzle which connects to the extruder. In other words, the whole system pressure was maintained similar as the pressure drop. As the solubility of CO<sub>2</sub> was increased with pressure drop, to different extents for different components, it was highly expected that cell nucleation in different phases in a polymer blend could be altered via adopting different nozzles. Thereby, different cell structures could thus be tuned.

The effect of pressure drop on the cell structures of PP, PS and PP70/PS30 foams prepared with 5.0 wt% scCO<sub>2</sub> and the corresponding cell densities are shown in [Figure 8: see original paper] and [Figure 9: see original paper], respectively. It has already been discussed in [Figure 6: see original paper] and [Figure 7: see original paper] that the difference of cell nucleation density in PP phase and PS phase in PP70/PS30 blend was responsible for the formation of bimodal cell structure of the foam prepared with Nozzle A (corresponding to a pressure drop of 10.5 MPa) and 5.0 wt% scCO<sub>2</sub>. When Nozzle B was applied (corresponding to a pressure drop of 13.0 MPa), the solubility of CO<sub>2</sub> in PP and PS at 165 °C were about 10.3 and 5.8 g/100 g, respectively [19,20]. The scCO<sub>2</sub> applied in the continuous extrusion was 5.0 wt%, which would completely dissolve in both PP and PS phases. As a result, the cell density in both phases was similar in PP70/PS30 foams ([Figure 9: see original paper]) and therefore no bimodal cell structure was formed ([Figure 8: see original paper]). Similarly, when Nozzle C was used (corresponding to a pressure drop of 18.0 MPa), the solubility of scCO<sub>2</sub> in PP and PS at 165 °C were about 18.0 and 7.7 g/100 g, respectively [19,20], both higher than the applied scCO<sub>2</sub> content. Similar cell density was formed in PP phase and PS phase in PP70/PS30 foams ([Figure 9: see original paper]), and eventually, no bimodal cell structure was formed ([Figure 8: see original paper]).

To further investigate the effect of pressure drop on the cell structures of PP, PS and PP70/PS30 foams, a parallel experiment was carried out with the applied scCO<sub>2</sub> changed to 7.0 wt%, and the results are shown in [Figure 10: see original paper]. As discussed in Section 3.4.1, when Nozzle A was applied, the PP70/PS30 foam prepared with 7.0 wt% scCO<sub>2</sub> showed a bimodal cell structure, due to the different cell nucleation between PP phase and PS phase. When Nozzle B was applied, the solubility of CO<sub>2</sub> in PP and PS was about 10.6 and 6.0 g/100 g, respectively [19,20]. The content of applied scCO<sub>2</sub> was 7.0 wt%, which was higher than its solubility in PS while lower than that in PP. Thus, the difference in cell nucleation in the two phases in PP70/PS30 foams led to formation of bimodal cell structure. In comparison, when Nozzle C was applied,

the solubility of CO<sub>2</sub> in PP and PS was about 18.4 and 8.1 g/100 g, respectively [19,20], both higher than the applied content of scCO<sub>2</sub>. Eventually, no bimodal cell structure was formed for PP70/PS30 foam prepared under this condition.

Based on the experimental results and discussions in this section, bimodal cell structures were formed in PP70/PS30 foams only when the dissolved content of scCO<sub>2</sub> in PP phase was prominently higher than that in PS phase. As the dissolved content of scCO<sub>2</sub> largely determines the cell nucleation, once again, it has proved that a prominent difference in cell nucleation is required in different phases in a polymer blend for the formation of bimodal cell structure, and that the cell nucleation could be altered through dissolving different contents of scCO<sub>2</sub>, which was achieved via changing pressure drop by adopting different nozzles.

### 3.4.3. Effect of Nucleating Agent on Cell Structures

It has already been discussed in [Figure 3: see original paper] that pure PP foam showed a higher cell density than pure PS foam, as PP has a larger affinity for CO<sub>2</sub>. scCO<sub>2</sub> under the experimental condition (165 °C, 5.0 wt% scCO<sub>2</sub>) in this study. Further, it was proposed that the formation of bimodal cell structures in PP/PS blend foams was dependent on a prominent difference in cell nucleation in PP phase and PS phase. Without incorporation of a heterogeneous cell nucleating agent, the difference in cell nucleation density in PP/PS blends could be dominated by the dissolved CO<sub>2</sub> content. Thus, it could be imagined that if a heterogeneous cell nucleating agent was incorporated into the PP/PS blends, the cell nucleation density formed in PP phase and PS phase would be increased while the difference between them would be reduced so that the bimodal cell structure could not be formed.

As previously reported [27-29], the clay could significantly enhance the cell nucleation of polymer melts as a heterogeneous nucleating agent through lowering the nucleation energy barrier. Therefore, the clay was applied to PP, PS and the PP/PS blends at a content of 1.0 wt% to investigate its effect on the cell structures of the foams, and the results are shown in [Figure 11: see original paper]. By comparison of the results in [Figure 11: see original paper] and [Figure 3: see original paper], several findings were worthy of being mentioned. First, the cell sizes of PP/clay foam ([Figure 11: see original paper]a) and PS/clay foam ([Figure 11: see original paper]b) were smaller relative to those of their counterparts without clay, due to the enhanced cell density with the incorporation of clay. Second, the decrease in cell size of PS/clay foam was more pronounced than that of PP/clay foam. It was probably due to that the heterogeneous nucleation was more prominent for PS than PP with the application of clay. Based on a reported study [30], PP has a high affinity for CO<sub>2</sub>, and the high content of dissolved CO<sub>2</sub> could enhance its cell nucleation ability. When the applied CO<sub>2</sub> in PP melts reached 5.0 wt% in content, the cell nucleation was mainly governed by CO<sub>2</sub>, while slightly affected by the addition of a heterogeneous nucleating agent. In comparison, for PS, its cell nucleation ability was

weaker due to its lower affinity for CO<sub>2</sub>. Thereby, the addition of clay could significantly improve the cell density of PS foam than PP foam, and hence, the cell size was decreased more prominently for the former. Third, no bimodal cell structure was formed for PP/PS/clay foams ([Figure 11: see original paper]c-f), and the cell sizes were similar for all the foams. It was interpreted that the cell nucleation density of PS phase was increased more than that of PP phase after incorporation of clay and thus the difference in cell nucleation between them was reduced to some extent where bimodal cell structure could not be able to form. For the cell size, Zhai et al. [31] reported that the heterogeneous nucleation by incorporation of nano-silica uniformized the originally broad cell size distribution of polycarbonate foam. Therefore, in this study, the cell sizes of the PP/PS blend foams could probably also be uniformized by the incorporation of clay as a heterogeneous nucleating agent.

To verify the changes in cell density of the foams with incorporation of clay and thus to confirm the aforementioned discussions, the cell density of pure PP, pure PS and PP/PS blend foams with and without clay was studied ([Figure 12: see original paper]). Several findings about the changes in cell density summarized below could well support the changes in structure of the PP/PS blend foams after incorporation of clay. First, the cell density of all the foams was increased. Second, the cell density of PS foam was increased more than that of PP foam. Third, the difference in cell density between PP phase and PS phase was significantly reduced. Therefore, the cell density data in [Figure 12: see original paper] could well support why no bimodal cell structure was formed in PP/PS foams with incorporation of clay.

Based on the results and discussions in this section, it was found that the incorporation of a heterogeneous cell nucleating agent could alter the formation of bimodal cell structure by changing the cell nucleation density in PP phase and PS phase to different extent. Thus again, it proves the proposed mechanism that a prominent difference in cell nucleation in different phases is necessary for formation of bimodal cell structure in a polymer blend, and that cell nucleation could be altered via incorporating a heterogeneous cell nucleating agent.

In summary, the difference in cell nucleation in PP phase and PS phase was considered to dominate the formation of bimodal cell structure of the binary polymer blends. If the cell nucleation ability for PP and PS was similar, or the difference was reduced, the bimodal cell structure could not be formed in the PP/PS blend foams. Thereby, from this perspective, the experimental results obtained via changing experimental conditions or adding clay could well support the proposed mechanism for formation of the bimodal cell structure.

#### 4. Conclusions

In this study, PP/PS blend foams with a bimodal cell structure were prepared in continuous extrusion foaming process with scCO<sub>2</sub> as the blowing agent. It was found that the large cells were mainly formed in PS phase, while the small

ones were mostly formed in PP phase. A possible mechanism was proposed to explain the formation of the bimodal cell structure that the difference in cell nucleation ability between PP phase and PS phase played a key role in dominating the formation of bimodal cell structure. Once the cell nucleation ability of PP and PS was altered by changing the experimental conditions, such as the content of scCO<sub>2</sub> and the pressure drop, or by adding a nucleating agent, the cell structure was changed. Therefore, it well confirmed the proposed mechanism that a large difference in cell nucleation ability was necessary for the formation of the bimodal cell structures in the binary polymer blends.

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