Effect of POE on mechanical properties and cellular structure of PP/Nano-CaCO₃ composites in IMD/MIM process

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Abstract

Nano-CaCO₃ can effectively improve the strength of foamed Polypropylene (PP), ethylene-octene copolymer (POE) can greatly enhance the toughness of PP, and PP-g-MAH can improve the compatibility of Nano-CaCO₃ with PP. The supercritical fluid-nitrogen (N₂) was used as physical foaming agent, and the PET film was selected to study the effect of POE content on the mechanical properties and cellular structure of PP/nano-CaCO₃ blends during combined in-mold decoration and microcellular injection molding (IMD/MIM) process. The results showed that the addition of POE did improve the impact strength of PP/nano-CaCO₃ composites, while the tensile strength and flexural strength decreased. On account of the characteristics of POE, the melt strength change of PP/nano-CaCO₃ blend system after POE’s addition was studied. The melt strength of the blend system decreased at first and then increased. It can be found that POE distributed uniformly in PP, and POE particle size decreased with the increase of POE content. Besides, it was revealed that POE could improve the cellular structure of the vertical section and the parallel section. The mechanical properties and cellular structure were optimized when 10% POE was added.

1. Introduction

Polypropylene (PP) has excellent properties such as light weight, good thermal stability, solvent resistance and easy processing, thus widely applied in many fields such as electrical equipment, automotive interiors, and furniture [1–3]. Microcellular foaming can make the polymer obtain a cellular structure with a cellular diameter of less than 10 μm and cellular density of more than 10⁹ cells/cm³ [3, 4]. Microcellular foamed polymer is a new material with lightweight, low electrical conductivity, high insulation and high dimensional stability [5–8]. However, there are inevitably some disadvantages of microcellular foaming products, such as low notched impact strength, low temperature brittleness, reduced tensile strength, and uneven cellular distribution [7–9].

In order to improve the mechanical properties and cellular morphology of microcellular foamed products, rigid particles and elastic particles were added to the polymer as nucleating agents. Polymers were enhanced by blending with rigid particles such as calcium carbonate and silica and fiber, etc [10–12]. And polymers got toughened by blending with elastic particles such as rubber particles, POE and EPDM, etc [13–16]. Mao studied the effect of nano-CaCO₃ content on the crystallization, mechanical properties and cellular structure of PP nanocomposites. It was found that the addition of nano-CaCO₃ improved the crystallization behavior, mechanical properties and cellular structure of microcellular foamed PP, and the mechanical properties and cellular structure were best when the content of nano-CaCO₃ was 6% [17]. Huang studied that HDPE and nano-CaCO₃ in PP improved the cellular structure of microcellular injection molding. It was revealed that when
HDPE was added to make the melt viscosity of PP/HDPE blend close to 1, the cellular size was the smallest and the cellular density was the largest. With the addition of 5% nano-CaCO3 to the PP/HDPE blend system, the cellular density reached the maximum [18]. Li studied the effect of nano-CaCO3 content on the foaming effect of short carbon fiber/polypropylene composites, and found that with the increase of nano-CaCO3 content, the average cellular diameter decreased first and then increased, and the cellular density showed the opposite trend [19]. Tang studied the effect of POE content on the mechanical properties of PP-R/POE blends, and found that POE could be used as a nucleating agent to induce the crystallization of PP at high temperatures. At 20% POE content, the impact strength of the composite was increased by 3 times due to the hole effect and the shear yield induced by POE [20]. Heidari used two different chemical foaming agents to study the effect of cellular structure on the impact strength of foamed materials. It was observed that the impact strength of foamed materials was directly related to the content of POE, and increasing the content of POE resulted in cellular size and wall thickness reduction [21]. Wang studied the effects of POE content, pressure, foaming temperature and number of layers on cellular size, apparent density, foamed rate and cellular density in different phase morphology. The results showed that the key to obtain a light PP was to adjust the foaming temperature so that the foaming of the SCF-CO2 in the PP/POE composite with different phase morphology occurred only in the POE phase [22]. Zhao studied the effect of rubber and talc on the mechanical properties of PP foamed materials. The results revealed that due to the toughened effect of rubber and the improvement of the cellular shape, PP/rubber foamed materials had higher ductility, while the talc particles significantly increased the rigidity of the PP/rubber foamed material, thereby obtaining a lightweight and strong PP/rubber/talc composite foamed material [23]. The combined in-mold decoration and microcellular injection molding (IMD/MIM) method improved the surface quality of the foamed parts [24]. Jungwoo studied the effect of different thickness of films on the surface quality by attaching an insulating PTFE film to the mold surface. It was observed that the surface quality of the foamed parts became better with the gradually increasing thickness of the PTFE film [25].

At present, there are a lot of researches on foaming after adding rigid particles or elastic particles to PP, but there are few studies on foaming after adding both rigid particles and elastic particles to PP, and even fewer systematic studies on foaming after adding nano-CaCO3 and POE to PP. Therefore, the effect of POE on the cellular structure and mechanical properties of the PP/nano-CaCO3 blend system was systematically studied from four aspects of mechanical properties, melt strength, particle micromorphology, and cellular structure, so as to obtain excellent comprehensive mechanical properties of foamed composite material, thus broadening the application prospect of foamed materials.

2. Experimental

2.1. Material

Polypropylene (K8303) with a melt flow index of 3 g/10 min was supplied by Sinopec Yanshan Co., Ltd (Beijing, China). Nano-CaCO3 with an average diameter of 60–80 nm was provided by China Changshan Golden Bear Co., Ltd (Changshan, China). Maleic anhydride grafted polypropylene (PP-g-MAH) as a compatibilizer with a graft ratio of 1.2% was provided by Dongyuan Ziheng Plastic Co., Ltd (Dongyuan, China). Industrial N2 (99% purity) as a foaming agent was provided by Wuhan Xiangyun Industrial Co., Ltd (Wuhan, China). The film used a polyethylene terephthalate (PET) film with a thickness of 0.2 mm, a thermal conductivity of 0.248 W m\(^{-1}\)K\(^{-1}\), and a surface quality of 2.6 μm. POE (DF640) with a melt flow index of 3.6 g/10 min was supplied by Singapore Mitsui Chemicals Management Co., Ltd (Singapore). Xylene, was commercially available.

2.2. Preparation of nanocomposites

In this experiment, six samples were set up. The first sample: PP; the second sample: PP + 6% nano-CaCO3 + 5% PP-g-MAH. Assumed that the blended system of the second sample is PP2, and the third to sixth samples were based on PP2, and add 5%, 10%, 15%, and 20% POE, respectively.

In the preparation process of the nanocomposite, the raw materials (PP, PP2, PP2 + 5%POE, PP2 + 10% POE, PP2 + 15%POE, PP2 + 20%POE) were dried by a drying oven (101A-1, Guangdi, Instrument Equipment Co., Ltd, Shanghai, China) for 8 h respectively, and the materials were stirred and mixed in a mixing stirrer (SHR-10, Yiyang Plastic Machinery Co., Ltd, Wuhan, China), put into a twin-screw extruder (SHJ-20, Giant Machinery Co., Ltd, Nanjing, China) for extrusion, and pelletized by pelletizer (LQ-20, Giant Machinery Co., Ltd, Nanjing, China). The temperature of the extruder barrel was from 190–190–190–200–200 °C. The composite masterbatch was dried in a drying oven at 80 °C for 24 h, and then placed in an injection molding machine (HDX50, Haida Plastic Machinery Co., Ltd, Ningbo, China) for sample preparation. The PET film was attached to the cavity side of the mold, and the temperature set of the injection molding machine was 190–200–200–190 °C, the injection pressure was 80 MPa, the back pressure was 10 MPa, the cooled time was 20 s, the gas injection pressure of nitrogen was 16 MPa, and the gas injection time was 3 s.
2.3. Microcellular foaming process
The schematic diagram of the process of microcellular foaming is shown in figure 1. SCF-N₂ was dissolved in the polymer solution to form a single-phase solution. When the melt was injected into the cavity of the mold, the thermodynamic instability was caused by the pressure drop, resulting in the gas saturated in the melt, which precipitated out of the melt and formed a large number of cellular nucleuses. The cellular nuclei were then continuously grown by constant diffusion of gas or cellular coalescence until reaching a state of equilibrium. Finally, the cells cooled and shaped, and a part of the cellular nucleuses smaller than the critical radius disappeared.

2.4. Characterizations
2.4.1. Cellular structure
In order to observe the cellular structure inside the spline, the flexural spline was cooled in liquid nitrogen for 3 h and immediately broken after taken out. The position of brittle fracture was shown in figure 2, and a sample with a length, width and height of 10 mm × 10 mm × 4 mm was obtained. Then, the obtained spline was cooled in liquid nitrogen for 3 h, and immediately broken after taken out. The parallel and vertical section (10 mm × 4 mm) were taken from the flexural samples, as shown in figure 2. A sample with a flat cross section was selected, and sprayed gold on the cross section, and then the morphology of the cells was observed with SEM (JSM-IT300, JEOL Ltd, Tokyo, Japan). Image pro plus was used to analyze the cellular data and count the size distribution of the cells.

The average diameter of the cells can be calculated by the following formula:

$$D = \frac{\sum_{i=1}^{n} d_i}{n}$$

Where: D is the average diameter of the cells, $d_i$ is the diameter of the cells of a single cell in a given area, and n is the number of cells.

![Figure 1. Schematic diagram of microcellular foaming process.](image1)

![Figure 2. Preparation of the vertical and parallel sections from the flexural sample.](image2)
The density of the cells can be calculated using the following equation:

\[
N = \left( \frac{n \times M^2}{A} \right)^{\frac{1}{2}}
\]

(2)

Where: \(N\) is the density of the cells, \(n\) is the number of cells in a given area, \(M\) is the magnification of the scanning electron microscope, and \(A\) is the area of the image.

For the parallel section of the parallel melt flow direction, the shearing force between the melts during the flow caused the deformation of the cells. The amount of deformation of the cells would be discussed here. The length-diameter ratio of the cells and the offset angle of the cells were used to characterize the amount of deformation of the cells. As can be seen from figure 3, when the length-diameter ratio of the cells was larger, the smaller the offset angle was, the larger the deformation amount of the cells was. The ratio of length to diameter \((d)\) was calculated by the following equation:

\[
d = \frac{b}{a}
\]

(3)

2.4.2. Melt strength

Later six foamed samples of PP, PP2 + 5%POE, PP2 + 10%POE, PP2 + 15%POE, and PP2 + 20%POE were incubated in the melt flow rate meter cylinder (MFI-1211, Chengde Jinjian Testing Instruments Co., Ltd Chengde, China) at 230 °C for 6 min. The experimental load was 2.16 Kg, and the melt was completely extruded from the capillary and a small portion of the melt would hang at the exit of the die. The time was recorded when the melt broke from the exit of the die, and the amount of the fracture was weighed four times for each sample. The data was interpolated to calculate the extrudate amount that could be suspended at the exit of the die for 30 s. The higher the measured amount, the higher the melt strength.

2.4.3. Microscopic morphology and distribution

In order to characterize the microscopic morphology and distribution of POE particles in the blend system, the flexural sample was cooled in liquid nitrogen for 3 h, and then broken immediately after taken out. A sample with a length, width and height of 10 mm × 10 mm × 4 mm was obtained at the position shown in figure 2. A sample with a flat cross section was selected, and etched in xylene solution at room temperature for 3 days in order to etch away the POE phase. The sample was taken out and sprayed gold to observe the cross section with SEM (JSM-IT300, JEOL Ltd, Tokyo, Japan).

2.4.4. Mechanical properties

The electromechanical universal test machine (CMT6104, MTS Systems Corp, Eden Prairie, MN, USA) was used to measure the tensile properties and flexural properties. The tensile test method was ISO 527-1:1993 with a...
crosshead speed of 50 mm min$^{-1}$. The flexural test method was ISO 178:2001 with a speed of 2 mm min$^{-1}$. The impact strength was measured by using an impact tester (XJUD-5.5, Chengde Jinjian Testing Instrument Co., Ltd, Chengde, China) according to ISO 180:2000. The values of all the mechanical properties were calculated as the average value of five specimens.

3. Results and discussion

3.1. Effect of POE content on mechanical properties

3.1.1. Tensile properties

It can be found from figure 4 that the tensile strength of PP2 was the largest, which was mainly because that the nano-CaCO$_3$ made the foamed material withstand a greater load when subjected to external force. At the same time, the added nano-CaCO$_3$ significantly improved the cellular structure and distribution, thereby improving the tensile properties. Due to the low strength of the PP melt, a large number of small cells collapsed and merged to form large cells, which became the stress concentration point, so the tensile strength was the lowest. Since the strength and modulus of POE were lower than PP, the tensile strength of foamed samples gradually decreased with the increase of POE content. When 5% POE was added, the tensile strength decreased the most, namely 10.7%. The main reason was that the strength of POE itself was low, and the cellular structure was deteriorated due to the decrease in melt strength.

3.1.2. Flexural properties

It can be found from figure 5 that the flexural strength of the PP2 was the largest. Because the strength of nano-CaCO$_3$ was higher than PP, and nano-CaCO$_3$ as a heterogeneous nucleating agent made the blending system obtain an excellent foaming effect, and the stability and flexural strength of the material was improved. Among them, the addition of PP-g-MAH improved the distribution of nano-CaCO$_3$. In pure PP, the flexural strength was small owing to the low strength of PP itself and its poor foaming effect. According to the mixing rules, the strength of the blending system decreased with the addition of POE, and as the POE content increased, the flexural strength of the foamed composite gradually decreased. When 5% POE was added, the flexural strength decreased the most, which was 16.9%.

3.1.3. Impact properties

The impact toughness of the foamed material was mainly related to the added particles and the foaming effect of the blending system. After the addition of POE, the elastomer POE was dispersed in the form of fine particles in the blend system. According to the craze–shear band theory, the dispersed phase POE particles acted as a large number of stress concentration points, which can induce the silver stripes and shear bands in the PP matrix when subjected to the impact load, and a large amount of impact energy was absorbed, thereby significantly improving the impact toughness. Besides, POE and nano-CaCO$_3$ also provided more nucleation sites, making the cellular density larger and the cellular size smaller, which greatly alleviated the damage of external force impact. It can be seen from figure 6 that when 10% POE was added, the impact toughness was the best because of the better foaming effect. In pure PP, the foaming effect was poor due to the low melt strength, and many large

Figure 4. Tensile test results: (a) Tensile stress–strain curve of foamed composite; (b) Tensile strength.
cells were formed, which easily caused stress concentration and the worst impact toughness. The schematic diagram of toughening was shown in figure 7:

3.2. Effect of POE content on melt strength
The foaming effect of the foamed material had a great relationship with the melt strength. Melt strength measurements can be characterized by measuring the amount of the melt suspended from the die of the melt flow rate meter during the time of the fracture. The greater the amount measured, the higher the melt strength of the foamed material was. The amount of material that could be withstood by different component foamed materials within 30 s was listed in table 1 below:

It can be seen from table 1 that PP showed the minimum amount of material of 0.3649 grams and had the smallest melt strength. After nano-CaCO3 was added, the amount of material became 0.4998 g, because the
nano-CaCO₃ as a rigid particle increased the melt strength. After the addition of POE, the melt strength of foamed materials decreased due to the low melt strength of the POE itself, but was still higher than that of PP. The melt strength gradually increased with the increasing POE content. As the content of POE with long chain branch increased, the entanglement of molecular chains between POE and PP became obvious, which led to an increase in melt strength [26].

3.3. Microscopic morphology and distribution of POE
The microscopic morphology, particle size and distribution of the particles in the blend system had a significant impact on the macroscopic mechanical properties and microscopic cellular structure of the composite. The non-foamed sample was etched by xylene to obtain the SEM image of the PP/POE/nano-CaCO₃ blend system. As shown in figure 8, the elastomer POE was etched away, showing a black round hole in the image, and the obvious spherical particles on the cross section were PP-g-MAH, the white irregular particles were nano-CaCO₃, and some gray pits were formed by the POE particles that had fallen off. It can be seen from the image with a magnification of 1000 that the distribution of POE in the PP matrix was relatively uniform, and the ‘sea-island’ structure was formed in the PP matrix, which was mainly because the compatibility of POE and PP was better. It can also be observed that as the content of POE particles increased, the size of POE particles gradually decreased. According to the viscosity principle of blending, under the same melt blending process, the smaller the difference in viscosity between the blended system and the dispersed phase was, the more favorable the refinement of the dispersed phase would be. When 5% POE was added, the adding amount of POE was less. Since the melt flow rate of POE was much lower than that of the nano-CaCO₃/PP blend, the viscosity of the PP/nano-CaCO₃/POE blend didn’t decrease significantly, and the difference in the melt viscosity of the POE was still large, which made the dispersion of POE particles difficult, and in this case, it was easy to obtain larger particles. As the content of POE continued to increase, the difference in melt viscosity between POE and blending system was reduced, which was beneficial to the uniform dispersion and refinement of POE particles. POE was dispersed in PP in the form of fine particles, and when subjected to impact load, POE acting as a stress concentration point, induced a large amount of silver streaks and shear bands in the PP matrix, and absorbed a large amount of impact energy through the continuous branching of the silver stripes. POE also acted to stop the silver stripes, but too small POE particles would be ‘submerged’ by the silver stripes, which wouldn’t stop the silver stripes. Nano-CaCO₃ agglomerates could be seen in the image of 20% POE at 5000 times magnification, because the excessively added POE content resulted in an excessive increase of the melt strength (viscosity) of the blend, which wasn’t conducive to the dispersion of nano-CaCO₃ particles during melt blending, leading to local agglomeration of the nano-CaCO₃ particles. When the number of elastic particles exceeded the critical value, the adjacent particles were too close to facilitate the generation of the silver stripes and the shear bands, and the foaming effect of the composite material was also deteriorated.

3.4. Effect of POE content on cellular structure
Since the cell vertical to the flow direction was hardly subjected to shear during the growth process, the cell parallel to the flow direction was subjected to a large shear action due to the melt flow. The morphology of the cells made the cross section vertical and parallel to the flow direction different, so we studied the cells of the vertical and parallel sections. And because the different cooling speed of the melt, we divided the vertical and parallel sections into 3 layers (2 transition layers, 1 core layer) for auxiliary research, as figure 9 showed.

3.4.1. The cellular structure of vertical section

3.4.1.1. Core layer of vertical section
Figure 10 is an SEM image of the core layer of the vertical section of the six samples, and it can be found that the foaming effect of PP was the worst, and that of 10% POE was the best. The foaming effect of the sample was closely related to the melt strength of the foaming system at the foaming temperature. Because PP had the lowest

| Table 1. Amount of material of different samples. |
| Sample serial number | Amount of material (g/30 s) |
|-----------------------|-----------------------------|
| PP                    | 0.3649                      |
| PP2                   | 0.4998                      |
| PP2 + 5%POE           | 0.4237                      |
| PP2 + 10%POE          | 0.4883                      |
| PP2 + 15%POE          | 0.6809                      |
| PP2 + 20%POE          | 0.8325                      |

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Figure 8. Corrosion diagram of non-foamed sample of PP2 + 5% POE, PP2 + 10% POE, PP2 + 15% POE, PP2 + 20% POE: (a)–(d) magnification 1000; (a′)–(d′) magnification 5000.
melt strength, with the cells growing, the cell walls were broken, causing adjacent cells to be connected together. Nano-CaCO$_3$ as a heterogeneous nucleating agent increased the melt strength and provided many nucleation sites, and the foaming effect was better than PP. After introducing 5% POE, the melt strength of the blended system decreased and the cellular structure became worse. When 10% POE was added, the melt strength increased, and POE acted as a heterogeneous nucleating agent, increasing the cell nucleation sites. Therefore, the cellular structure was the best. After adding 15% and 20% POE, the content of POE was too large. On the one hand, the sizes of the POE dispersed phases were smaller and closed to each other and the cells coalescence was likely to occur during the foaming process, resulting in poor foaming effect. On the other hand, the melt strength (viscosity) was too large, and local agglomeration of nano-CaCO$_3$ occurred, which deteriorated the cellular structure.

As shown in figure 11, in PP, due to the collapse and combination of the cells, there were many cells with a diameter of 160 $\mu$m or more, and the cellular size distribution was poor, and the cellular diameter variance was 3214.9. After the addition of nano-CaCO$_3$, the cellular diameter distribution became better, the cellular diameter variance was 1023.8, the number of big cells decreased, and the cellular size distribution became concentrated. The cellular size was mainly 60–110 $\mu$m. With POE added, there were some changes in the cellular size distribution. When 5% of POE was added, the number of large cells increased, and the distribution of cells was poor, with a variance of 1431.5. Compared with PP2, 10% POE also improved the cellular distribution, in which the variance was 753.5, the cellular size distribution was also concentrated, and the small cells with a cellular diameter of 60–100 $\mu$m were obviously increased. With the increase of POE content, the cellular size...
The average cellular diameter and cellular density can be calculated using Image Pro Plus software.

As can be seen from figure 12, the cellular density was the highest at 10% POE, reaching $33.8 \times 10^9$ cells cm$^{-3}$, which was greatly improved compared with $9.1 \times 10^9$ cells cm$^{-3}$ of PP and $23.2 \times 10^9$ cells cm$^{-3}$ of PP2, increasing by 271% and 45.7% respectively. The main reason was that the POE content at this time allowed the blend to maintain a high melt strength and provided a large number of heterogeneous nucleation sites. In 15% and 20% POE, the foaming effect was poor due to the excessive addition of POE, so the cellular density decreased. In PP2, nano-CaCO$_3$ increased the melt strength and provided nucleation sites with cells, with an average diameter of 85.94 $\mu$m. The average diameter of the cells and the cellular density changed in the reverse direction. The average cellular diameter of 10% POE was 81.8 $\mu$m, and that of PP was 116.88 $\mu$m.

3.4.1.2. Transition layer of vertical section
The bottom transition layer structure of different samples is as shown in the figure 13 (the bottom transition layer is similar to the top transition layer). This paper studied a bottom transition layer.
Figure 13. Transition layer cellular structure of vertical sections of different samples: (a) PP; (b) PP2; (c) PP2 + 5% POE; (d) PP2 + 10% POE; (e) PP2 + 15% POE; (f) PP2 + 20% POE.

Figure 14. Distribution of transition layer cellular sizes for vertical sections of different samples: (a) PP; (b) PP2; (c) PP2 + 5% POE; (d) PP2 + 10% POE; (e) PP2 + 15% POE; (f) PP2 + 20% POE.

Figure 13 illustrated the cells of the transition layer were smaller than that of the core layer, which was mainly because the melt of the core layer was cooled slowly, the cells had more time to grow. The transition layer was closed to the mold, the cooled rate was faster, and the size of the cell was small.

It can be seen from figure 14 that the cellular size distribution of the vertical cross-section transition layer was similar to that of the core layer. The variance of the cellular diameters of 5%, 10%, 15% and 20% POE were 392.3, 290.1, 351.8, and 689.9, respectively, and the variance of 10% POE was the smallest. At 10% POE, the distribution of cells was the most concentrated, and the small cells with a diameter of 40–70 μm were the most.

As shown in figure 15, the regularity of the average cellular diameter of the vertical section transition layer and the density of the cells were similar to those of the core layer. The main difference was that the average diameter of the cells reduced and the cellular density increased.

3.4.2. The cellular structure of parallel section

3.4.2.1. Core layer of parallel section

As figure 16 shows, the cells in FP wasn’t uniformly distributed, and there appeared some large cells. With the addition of nano-CaCO₃, the cellular distribution was more regular, and the cellular density increased. After adding 5% POE, the cellular structure became worse. When 10% POE was added, the cellular distribution and
morphology were further improved. When it went on increasing to 15% and 20% POE, the cellular structure deteriorated again due to excessive POE content.

As shown in figure 17, the distribution of the cellular size of the parallel section transition layer in PP was relatively dispersed, and there were many large cells with a diameter of 200–280 μm. By adding nano-CaCO₃, the distribution of cellular size became concentrated, and most of the cells were at 100–140 μm. After POE was added, the distribution of cellular size first deteriorated, and it became better in 10% POE, with most of the cells in the range of 80–120 μm, and then continued to deteriorate, mainly because of the influence of the melt strength and heterogeneous nucleation sites point.

Figure 18 shows that the average diameter of the cells in the core layer of the parallel section and the density of the cells changed similarly to the core layer of the vertical section. In 10% POE, the cellular density was the largest, 30.7 × 10⁹ cells cm⁻³, and the average cellular diameter was the smallest, 99 μm, for the reason as described above. However, it can be found that the average diameter of the cells in the core layers of the parallel section was larger than that of the vertical section, and the density was small, mainly because the cells were subjected to some shear action during the melt flow filling process, and the cellular diameter was enlarged.

3.4.2.2. Transition layer of parallel section

As is shown in figure 19, the shape of cells in the transition layer of the parallel section and that of the vertical section were completely different, because in the melt filling process, the cell was deformed by the shear stress
during nucleation and growth, and the cell changed from a circle to an ellipse. The length-diameter ratio of the transition layer cells and the offset angle of the cells could be used to characterize the deformation of the cells to some extent. The large length-diameter ratio and the small offset angle meant a large amount of deformation. In this paper, the average diameter of the cells of the parallel section transition layer wasn’t studied, because the cells were deformed by shear, and it was meaningless to study the diameter changes of different groups at this time.

As shown in Figure 20, the cellular density of 10% POE was the largest, which was $31.7 \times 10^9$ cells cm$^{-3}$. Compared with PP, the length-diameter ratio of the cells in PP2 became larger, and the offset angle of the cells became smaller, which indicated that the amount of deformation of PP2 of cells was large. The main reason was that with the addition of nano-CaCO$_3$, the resistance of the polymer melt molecular chain increased as it flowed, resulting in an increase in melt viscosity and an increase in the shear force of the cells. At the same time, due to the increased density of the cells, the thickness of the cellular walls decreased, and the ability of the cells to undergo deformation was reduced, leading to an increase in the amount of cellular deformation. In 10% POE, the cellular length-diameter ratio was the largest, and the offset angle was the smallest, so the deformation amount was the largest. It was because the POE with long chain branching continued to increase the resistance of molecular chain motion, the viscosity continued to increase, and the cell was subjected to the largest shear. At
this time, the density of the cells was the largest, the cellular walls were the thinnest, and the ability of the cells to undergo deformation was minimal. When adding a certain amount of POE, the density of the cells was reduced, meaning that the thickness of the cellular walls was increased, so the amount of deformation of the cells was reduced.

4. Conclusion

The effect of POE content on the mechanical properties and cellular structure of PP/nano-CaCO₃ foamed composites were investigated using combined in-mold decoration and microcellular injection molding (IMD/MIM) method. The results showed that acting as a heterogeneous nucleating agent, POE particles improved the cellular structure by changing the melt strength of the composite material, thereby significantly increasing the impact strength of the foamed composite material. However, due to the low strength and modulus of POE, the tensile strength and flexural strength decreased slightly. When 10% POE was added, POE was evenly dispersed in the PP/nano-CaCO₃ matrix, and had a higher particle density and a smaller particle size to obtain the best foaming effect and the highest impact strength, while tensile strength and flexural strength were also higher than pure PP foamed materials. Therefore, the addition of 10% POE particles in the PP/nano-CaCO₃ matrix obtained a foamed material with excellent comprehensive mechanical properties, which expanded the application of foamed materials in various industries.
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Author contributions

Formal analysis, W G and Z M; Investigation, H M and Y C; Software, Q Y; Supervision, L H and W W; Writing —original draft, Y C.

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Conflicts of interest

The authors declare no conflict of interest.

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