

The Interaction between Crystallization Behavior and Foaming Performance in the Foamed Polypropylene

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ABSTRACT

Three types of polypropylene, namely homo-polypropylene (HPP), block copolymer of propylene with ethylene (CPP-B) and random copolymer of propylene with ethylene (CPP-R) were melted and foamed in a self-designed vessel under supercritical carbon dioxide (Sc-CO₂) atmosphere. The melting behavior, crystalline forms and foaming performance of foamed samples were investigated using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and scanning electron microscope (SEM). The results showed that foaming process parameters greatly influence the crystallization behavior and foaming performance of samples. With the increasing of polypropylene contents, crystallinity, cell density was increased. Furthermore, under the certain critical condition, CO₂ can induce the change of crystal structure and β -crystals were obtained. In addition, it was observed that γ -crystals could be obtained in the foamed CPP-R under Sc-CO₂, while no γ -crystals were formed in the other two samples.

KEYWORDS: *Polypropylene, Crystalline forms, Foaming performance, Supercritical CO₂.*

INTRODUCTION

The crystallization and foaming of polypropylene (PP) with supercritical CO₂ (Sc-CO₂) have attracted tremendous attention in academic circles during the past several decades.^[1,2] PP is a kind of typical semi-crystalline polymer

and α -crystal is the main type in all crystal forms. Other two types (β -crystals^[3] and γ -crystals^[4]) crystals could only be obtained under the specific crystallization conditions. The β -crystals have kept enthralling research due to its excellent performance. It can not only play

a critical role on improving the toughness of PP^[5-7] but also can greatly increase the heat distortion temperature, which could be increased by 10°C to 25°C than α -crystals.^[8] The crystallization behavior has a critical influence on cell nucleation, growth and final form in the foaming process of PP. The original crystallization time and rate will affect the nucleation process. In the steadily growing stage of the cell, the crystallization behavior of PP imposed a significant impact on melt strength and melt elasticity. Appropriate melt strength can guarantee the stable growth of the cell and prevent cell from collapsing. In cooling and shaping stage, lower temperature can accelerate crystallization behavior, at the same time, crystallization time and rate play a significant role on the eventual quality of foamed products.^[9]

With supercritical CO₂ (Sc-CO₂) as foaming agent to prepare plentiful foamed plastics has kept receiving considerable attention because Sc-CO₂ has many desirable attributes, such as non-toxicity, easy availability, environmentally benign and moderate critical conditions. Thus it has been widely used in polymer processing areas.^[10] It is now well established that the dissolved CO₂ can plasticize polymer by increasing the free-volume fraction and the mobility of the molecular chains. Consequently, the crystallization temperature and glass transition temperature were depressed due to its plasticization effect^[11-17]. Besides these, CO₂ can also play the role of heterogeneous nucleation in the foaming process of crystalline and semicrystalline polymers. Ping Zhang et al.^[18] used Sc-CO₂ extrusion foaming PP to study the crystallization behavior and cell form. The

results showed that foaming temperature and pressure have certain relation with the melt viscosity and CO₂ solubility. DSC curves showed that CO₂ can increase the foamed PP melting peak and widen the melting temperature range. The melting point and crystallinity were decreased with the increase of foaming temperature, but were improved with the increase of foaming pressure.

Furthermore, some researchers studied the crystallization and foaming behavior of the blending systems, which contained polypropylene and other components. Wei Liu et al.^[19] studied the blending system of PP/LDPE. The results showed that polyethylene component has a great influence on the crystallization behavior and the cell growth process of PP. Wentao Zhai et al.^[20] studied the blending system of PP/Nano-clay, found that Sc-CO₂ can carry on the plug to the nano-clay layer and strip, adding nano-clay can increase the melt strength of the system and raise the foaming performance. Chunling Xin et al.^[21] studied the blending system of PP/UHMWPE, under the action of Sc-CO₂, using the ultra-high molecular weight polyethylene (UHMWPE) can enhance the crystallization temperature and relative crystallinity of polypropylene (PP) and expand the crystallization temperature range. UHMWPE played an effect on the crystallization behavior of PP and also changed the foaming performance of the blend, the cell density and foaming ratio were increased in a certain degree.

Although studies of the crystallization behavior and foaming performance of PP and the other compounds under CO₂ have been reported, as mentioned above, there is still no specific

research on the interaction between crystallization behavior and the foaming performance of polypropylene copolymer under Sc-CO₂. In this article we described comparative studies on the crystallization behavior and foaming performance of HPP, CPP-B and CPP-R under Sc-CO₂ atmosphere. The influence of foaming conditions (including temperature, CO₂ pressure) on the interaction between crystallization behavior and the foaming performance in these three types of PP was particular focused.

EXPERIMENTAL

Materials and Sample Preparations

A commercial homo-polypropylene (trade name HPP T30S, kindly supplied by Maoming Sinopec Corp., China.) was used in this study. The melt flow rate (MFR) was 3.0g/10min measured at pressure 2.16 kg and 230°C. The block copolymer of propylene with 8wt% ethylene monomer (CPP-B B380G) and random copolymer of propylene with 2wt% ethylene monomer (CPP-R R520Y) were also kindly supplied by SK Global Chemical Co., Ltd. (South Korea). The MFRs of the sample were 28.0g/10min and 1.8g/10min, respectively. Carbon dioxide (CO₂) with a purity of 99.9%, was obtained from Golden Zhujiang Gas Corp., China. All chemicals were used as-received. Three types of PP were moulded into 4 mm thick sheets in the plate vulcanizing machine (Dongguan Kesheng, Corp., China) at 200°C and 10 MPa for 6 min. Then the sheets of the samples were cut into 10×5mm pieces for the foaming experiment.

Foaming Process of Polypropylene/CO₂ System in Different Conditions

At the beginning of a foaming experiment, one 10×5mm piece of sample was put into a stainless steel high-pressure vessel and sealed, meanwhile a positive-displacement syringe pump (model 260D, Teledyne Isco, USA) was connected to inject high-pressure Sc-CO₂ into it. Before opening the inlet valve to make pressure

maintained predetermined value, CO₂ was used to rule out the air in the vessel for 3 times. Subsequently, the vessel was immersed into an oil bath at 190°C for 30min to ensure that HPP/CO₂ or CPP/CO₂ can form homogeneous system, then the vessel was rapidly moved to another oil bath at 135~155°C to be saturated 30min. After pressure foaming by opening the pressure relief valve in different depressurization rates, the vessel was moved into ice water bath at 4°C for 15min to fix the cell structure of foamed samples. For a reference, unfoamed PP samples were analyzed in the same conditions.

Differential Scanning Calorimetry (DSC) Measurements

The thermal performance of foamed PP samples were studied by using a differential scanning calorimeter (DSC204C, Netzsch Group, Germany). In the process of the experiment, nitrogen was used as a purging gas at a flow rate of 20 ml/min. The samples were heated from room temperature to 210°C with a heating rate of 10°C/min, and the endothermic heat flows were recorded as a function of temperature.

Scanning Electron Microscope (SEM) Measurements

The microstructure of foamed PP samples were studied by using a Scanning Electron Microscope (SEM Quanta200, FEI Group, America), the samples were cryo-fractured in liquid nitrogen to obtain the fracture surface. Fracture surface and abraded surface were coated with gold for observing morphology by scanning electron microscope (SEM). The cell density and cell diameter could be obtained from SEM, by using cell density and cell diameter to calculate foaming ratio.

Cell density, ρ_c the number of cell in the unit volume of foamed plastic, can be calculated from the SEM images.

$$\rho_c = \left(\frac{nM^2}{A} \right)^{\frac{3}{2}} \quad (1)$$

Where A is the area of the SEM image, M is magnification times and n is the number of cell in this area.

Cell diameter, d_c , by using image analysis software (image Pro Plus) to count the cell diameter of SEM

images.

$$d_c = \frac{d_s}{N} \quad (2)$$

Where d_s is the sum of the diameter of the different directions in this area, N is the diameter numbers.

Foaming ratio, φ , is the ratio between the foamed sample volume and unfoamed sample volume.

$$\varphi = \frac{V_2}{V_1} = \frac{\rho_1}{\rho_2} \quad (3)$$

Where V_1 and ρ_1 are the volume and density of unfoamed sample, respectively. V_2 and ρ_2 are the volume and density of being foamed.

Wide-Angle X-Ray Diffraction (WAXD) Measurement

The crystal forms of foamed PP samples were investigated by using an X-ray diffractometer (D8 ADVANCE, Bruker, Germany). The $\text{CuK}\alpha$ radiation source was operated at 40 kV power and 40 mA current. The experimental data was collected in a scan mode of $1^\circ/\text{min}$ within the range of $5^\circ\sim 30^\circ$ (2θ). The samples for WAXD analysis were $100\ \mu\text{m}$ thin slices which were sectioned from the foamed samples using a Leica (RM2235 rotary microtome Germany). PP is a typical homogeneous polycrystalline,^[22, 23] which presents more than one crystal structure, including mainly α -crystals, β -crystals and γ -crystals. Table 1^[3] lists Wide Angle X-ray Diffraction peak 2θ angle of the PP different crystal forms.

TABLE 1. Wide Angle X-ray Diffraction peak at different 2θ angles of PP

Crystal Form (crystals)	Angle 1($^\circ$)	Angle 2($^\circ$)	Angle 3($^\circ$)	Angle 4($^\circ$)	Angle 5($^\circ$)	Angle 6($^\circ$)	Angle 7($^\circ$)
α	14.0	16.8	18.6	21.2	21.8	25.5	28.5
β	16.0	16.6	21.0	24.7	28.1	-	-
γ	13.8	15.1	16.7	20.1	21.2	21.9	-

RESULTS AND DISCUSSION

Thermal Performance and Microstructure of Foamed PP at Various Foaming Temperature

Figure 1 showed the melting curves of PP samples unfoamed and foamed at various temperature, 155°C , 150°C , 145°C , 140°C , respectively, and foaming pressure was kept in 16 MPa. With the reduction of foaming temperature, foamed samples melting point showed a decreasing trend in Sc-CO_2 atmosphere, as CO_2 can plasticize polymer by increasing the free-volume fraction and the mobility of the molecular chains. The double melting peaks appeared in the melting curves of HPP and CPP-B at 155°C and 150°C ,

respectively. The foaming process has an obvious effect on crystallization behavior, especially to the crystal structure and crystal morphology has a relatively strong influence, which can be seen from the XRD curves. However, under the same crystallization temperature condition, there were no double melting peaks appeared in ordinary N_2 atmosphere and the different pressure of CO_2 crystallization. Namely, foaming process played a crucial effect on crystallization behavior. Furthermore, the crystallinity of foamed samples was also significantly increased at the two temperatures. Besides, compared with the melting curve of CPP-B, there were no double melting peaks in the melting curve of CPP-R under Sc-CO_2 action,

owing to the lack of longer and complete propylene chain segments in CPP-R. Random distribution of ethylene chain segment hindered the CO₂ from playing an influence on crystalline microstructure of the polypropylene at high foaming temperature. Namely, in CPP-B, a long ethylene chain embedded the main chain of

PP, has no effect on chain regularity. In CPP-R, random distribution of ethylene short chain has a critical role on whole structure.^[5, 6]

Figure 2 showed the microstructure of foamed samples from SEM images. It can be seen that, the cell density increased gradually, with

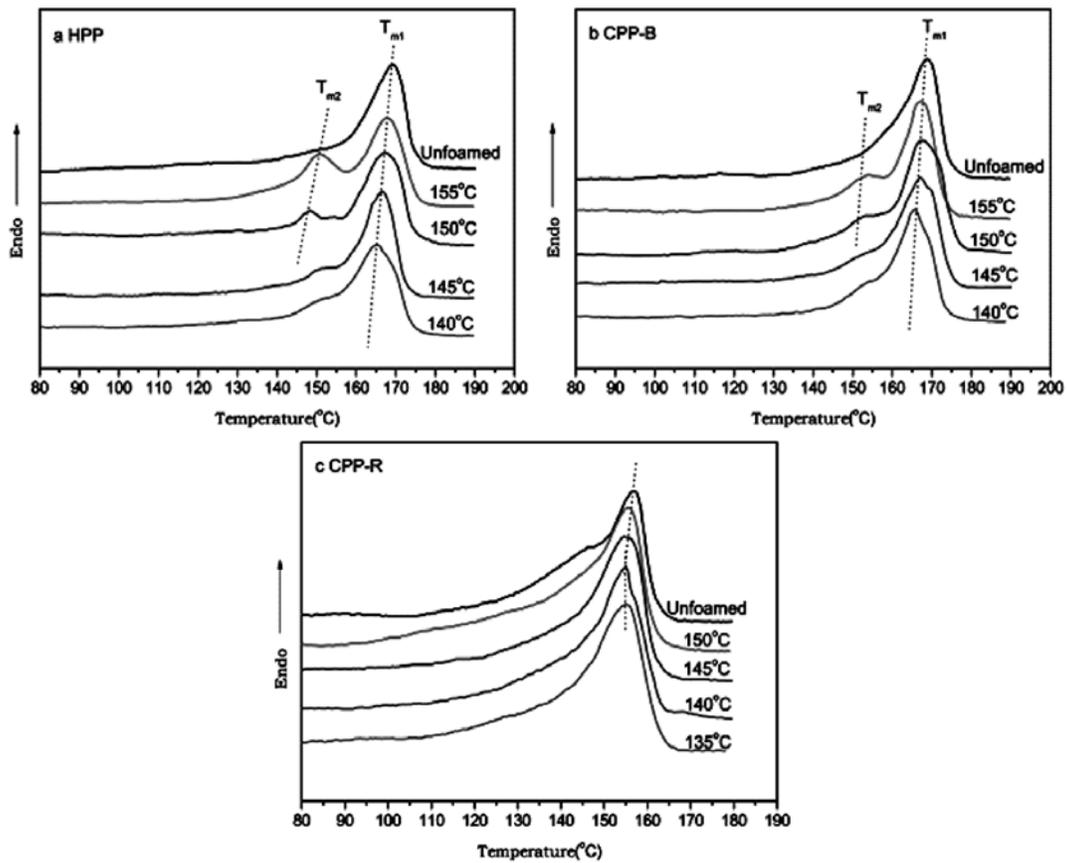


Fig. 1. DSC melting curves of foamed PP at various temperature (a:HPP, b:CPP-B, c:CPP-R)

the rising of foaming temperature, cell diameter became smaller and cell size distribution was more uniform. These are very favorable conditions for the formation of microcellular foam.^[25] From the SEM images of two foamed

PP (HPP, CPP-B), they all have one common feature, namely, the crystallinities were increased when foamed at 155°C. They showed the double melting peaks, which is indicated by the change in the crystal morphology.

Compared to CPP-B, the isotacticity of HPP was higher. This helps in the entry of CO₂ into the molecular chain layer in the foaming process, resulting in the change of the crystallization behavior and crystal structure.^[23-25]

Thermal Performance and Microstructure of PP Foamed at Various Foaming Pressure

Figure 3 showed the melting curves of PP samples at various pressure, 16MPa, 18MPa, 20MPa and 22MPa, respectively, and foaming

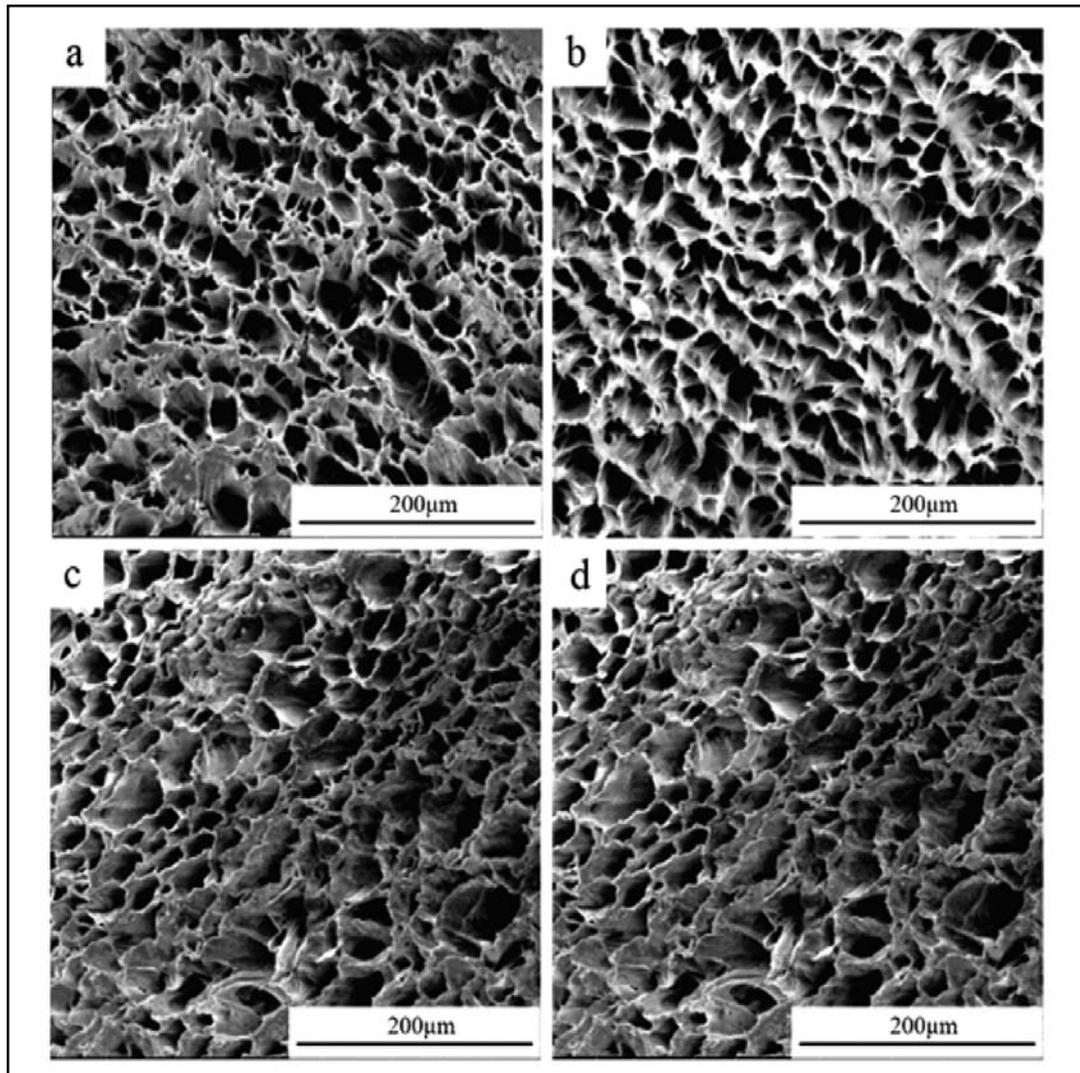


Fig. 2. The SEM images of foamed CPP-B/CO₂ system at various foaming temperature (a:150°C, b:145°C, c:140°C, d:135°C)

temperature was kept in 145°C. It can be seen that as the CO₂ pressure increases, the melting point of foamed HPP decreases but crystallinity enhanced. This can be attributed to the plasticization effect of CO₂. Furthermore, the melting curve showed the double melting peaks in 22MPa. This is due to change in the crystal structure and crystal morphology. There were no double melting peaks in foamed CPP-R, the melting peak platform was widened obviously under 22MPa, which also indicated the crystal structure and crystal morphology were changed in CPP-R.

Figure 4 showed the microstructure of foamed samples from SEM images. With the increase of CO₂ pressure, cell diameter showed a small change and cell density enhanced constantly, especially under the 22MPa. The pressure effect was more significant to the promotion of cell density. The same phenomenon could be seen in the SEM images of foamed HPP. The increasing of CO₂ pressure, causes in the improvement of crystallinity especially the microcellular foaming performance.^[9, 25]

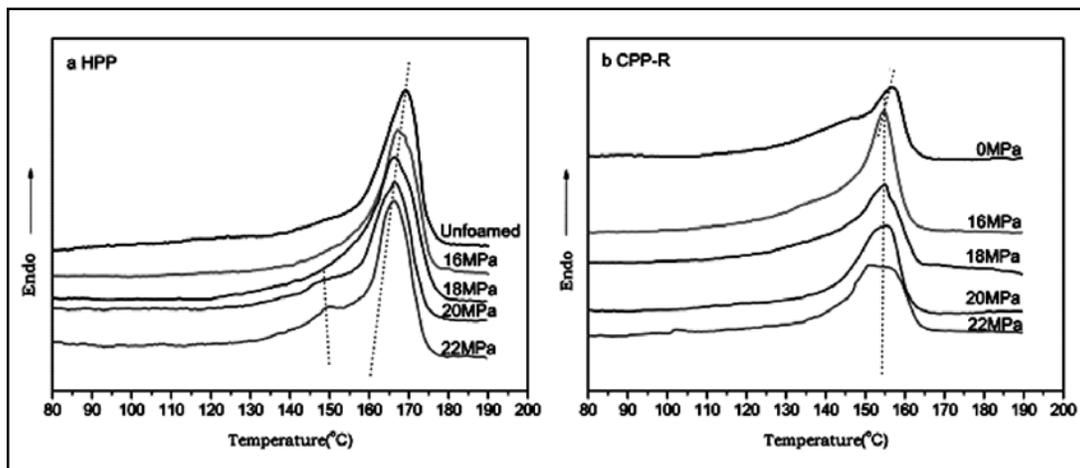


Fig. 3. DSC melting curves of foamed PP at various foaming pressure (a:HPP, b:CPP-R)

Crystalline Structure of Foamed PP at Various Foaming Processes

It can be seen that the double melting peaks appeared in the melting curve of foamed PP, which showed the change of crystal structure and morphology XRD results. Fig. 5 showed β -crystals were induced under higher foaming temperature and lower pressure in the system of HPP/CO₂, especially at 155°C. According

to the formula(4) the content of β -crystals was 31.7%. At 150°C β -crystals content was 13.6% but there was no β -crystals appeared at temp below 150°C end CO₂ pressure at 16MPa. At 145°C and pressure 20MPa, β -crystals could be obtained again. According to the work mentioned previously about β -crystals,^[6] molecular chain structure, temperature, stress field and nucleating agent have essential effects on formation of β -crystals. The relative amount

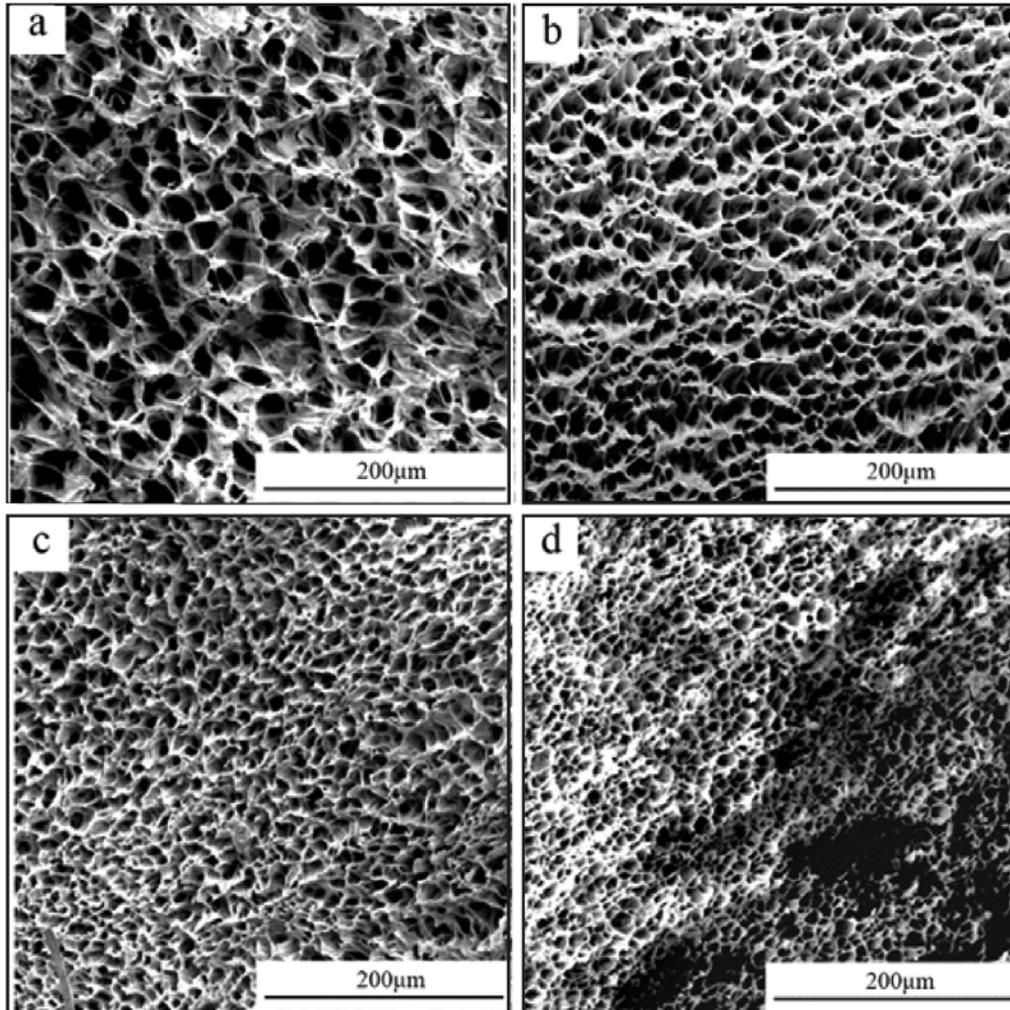


Fig. 4. The SEM images of foamed CPP-R/CO₂ system in various pressure (a:16MPa, b:18MPa, c:20MPa, d:22MPa)

of β -crystals, $G(\beta)$, γ -crystals, $G(\gamma)$ were calculated according to Equ.4 and Equ.5 suggested by Turner-Jones.^[26]

$$G(\beta) = \frac{H(\beta)}{H(\beta) + H(\alpha_1) + H(\alpha_2) + H(\alpha_3)} \quad (4)$$

Where $H(\beta)$ and $H(\alpha_1)$, $H(\alpha_2)$, $H(\alpha_3)$ are the diffraction intensities of β (300) and α (110), α (040), α (130) planes at diffraction angles $2\theta = 16.0^\circ$ and 14.0° , 16.8° , 18.6° , respectively.

$$G(\gamma) = \frac{H(\gamma)}{H(\gamma) + H(\alpha_3)} \quad (5)$$

Where $H(\gamma)$ and $H(\alpha)$ are the diffraction intensities of $\gamma(117)$ and $\alpha(130)$ planes at diffraction angles $2\theta = 20.1^\circ$ and 18.6° respectively.

We could draw the conclusion that under the certain foaming conditions, CO_2 can penetrate into PP molecular chain layer and produce a strong effect on the crystallization behavior of PP which not only changed the melting point and crystallinity but also changed crystal structure to induce α -crystals. Namely, sheared field produced during PP melt process can induce β -crystals nucleation (α -row nuclei) and to further promote the transformation α -to- β under appropriate crystallization conditions. In turn, β -crystals greatly improved the crystallinity

and enhanced the crystallization performance of PP, thus affected the foaming performance of PP and improved the cell density of foamed samples.

Figure 6 showed the XRD curves of foamed CPP (CPP-R and CPP-B) with double melting peaks. It can be seen that the high foaming temperature and pressure can promote the generation of β -crystals, however, the content of β -crystals were less than the HPP/ CO_2 system, the reasons may be that there has the ethylene chain segment in the CPP. According to the work mentioned previously in the same crystallization condition, HPP can more easily form β -crystals than CPP because the formation of β -crystals need relatively uniform chain structure.^[5, 6]

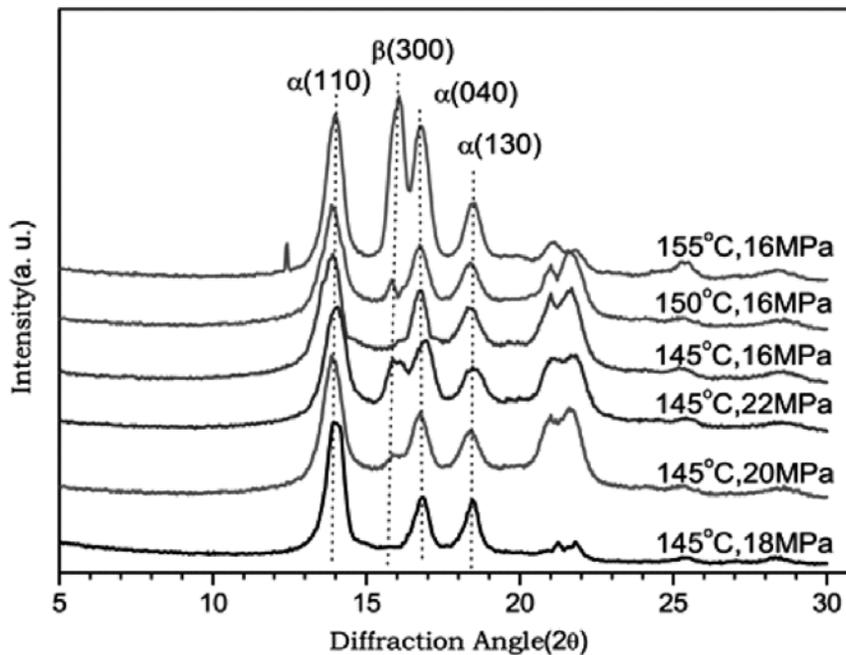


Fig. 5. The XRD curve of foamed HPP with double melting peaks

TABLE 2. % of different crystals content of foamed HPP/CO₂ under different foaming conditions

Foaming conditions (temperature pressure)	The content of α -crystals	The content of β -crystals
145°C, 16MPa	100%	0%
150°C, 16MPa	86.4%	13.6%
155°C, 16MPa	68.3%	31.7%
145°C, 18MPa	100%	0%
145°C, 20MPa	88.1%	11.9%
145°C, 22MPa	77.5%	22.5%

The characteristic peaks of γ -crystals could be seen in the XRD curves and the content of γ -crystals increased with the rising of pressure. The results showed that γ -crystals were easier

induced than β -crystals under the higher foaming pressure.^[27-30] Table 3 showed the specific content of the crystals in foamed CPP/CO₂ system.

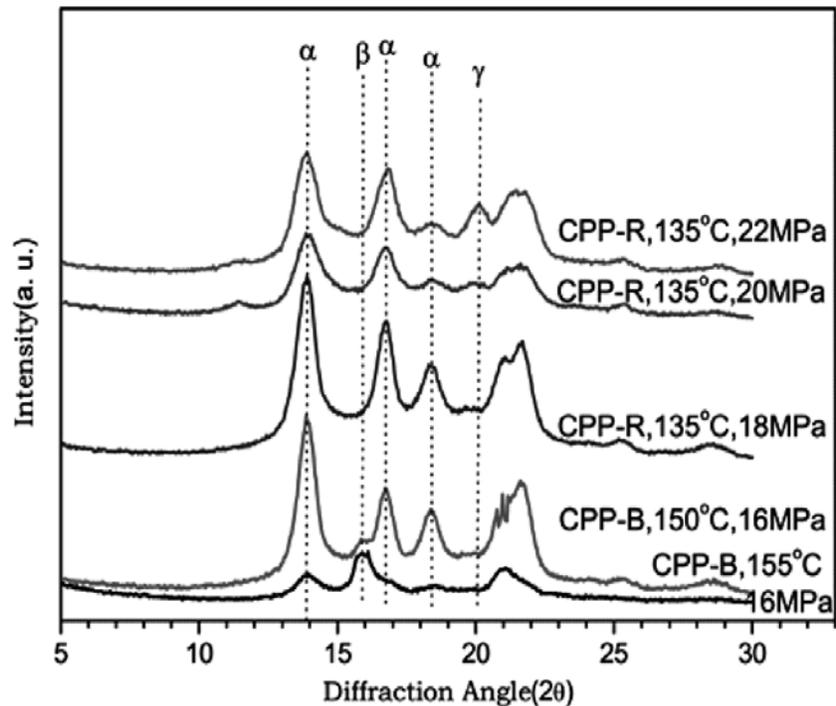


Fig. 6. The XRD curves of foamed CPP with double melting peaks

TABLE 3. The crystals content of foamed CPP/CO₂ system in different foaming conditions

Foamed conditions	Foaming conditions (temperature pressure)	The content of α -crystals	The content of β -crystals	The content of γ -crystals
CPP-B	155°C, 16MPa	79.9%	20.1%	0%
	150°C, 16MPa	89.2%	10.8%	0%
CPP-R	135°C, 18MPa	100%	0%	0%
	135°C, 20MPa	66.6%	0%	33.4%
	135°C, 22MPa	41.5%	0%	58.5%

CONCLUSION

In this study, the interaction between crystallization behavior and foaming performance of three types polypropylene (PP) with the presence of Sc-CO₂ was investigated. It was observed that different foaming process have a critical influence on the crystallization behavior and foaming performance of PP. Specifically, under the foaming temperature of 150°C and the pressure of 16MPa, CO₂ can induce HPP to produce β -crystals and the induction-effect was increased with the increase of temperature. According to the work mentioned previously about β -crystals, molecular chain structure, temperature, stress field and nucleating agent have essential effects on formation of β -crystals. Selecting suitable melting crystallization temperature and creating certain temperature gradient were valid to induce β -crystals in PP. In addition stress field played an important role on forming β -crystals by imposing dynamic change on the melt. It has already been approved that sheared field produced during PP melt process can induce α -crystals nucleation (α -row nuclei) and to further promote the transformation α -to- β under appropriate crystallization conditions. In turn, under the foaming temperature of 145°C

and the pressure increased more than 20MPa, the system also can be induced to produce β -crystals and the induction-effect was increased with the increase of pressure. For the three types of foamed PP, the crystallization behavior and the foaming performance were closely related, the cell density of foamed samples were increased with the increase of crystallinity and cell size was more uniform, which greatly improved the foaming performance in a certain range. The characteristic peaks of γ -crystals could be seen in the XRD curves and the content of γ -crystals increased with the rising of pressure.

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