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Foaming of Polystyrene with Supercritical Carbon Dioxide

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Abstract: General Purpose Polystyrene (GPPS) and High Impact Polystyrene (HIPS) were foamed with supercritical carbon dioxide in the batch foaming process. Foaming behaviors of GPPS and HIPS were investigated. The cell diameters and cell densities of GPPS and HIPS vary strangely with foaming conditions and can not be explained by the classical nucleation. The competition between cell growth and cell nucleation is used to explain these strange foaming behaviors. The glass transition temperature (T_g) almost remains constant with the foaming temperature rising.

1 Introduction

In recent years, the applications of supercritical carbon dioxide ($scCO_2$) have been prompted in polymer products and in polymer processing. Plastic foams represent a group of lightweight materials that have been widespread used in a variety of industries. Environmentally benign gases such as $scCO_2$ are attractive physical blowing agents in which microcellular foams can be formed that provide high performance products. The foamed polymer materials may be characterized by outstanding properties such as high impact strength [1], high toughness [2], high stiffness-to-weight ratio [3], high fatigue life [4], high thermal stability [5], low dielectric constant [6] and low thermal conductivity [7] as well as reducing costs. Therefore, they find many potential applications such as food packaging, automotive cars, refrigerator linings insulation, and sporting equipment, etc. [8].

Now many kinds of microcellular polymers have been successfully prepared, and Colton's classical nucleation theory is widely accepted and used. However, the results from other researchers indicate that classical nucleation theory is not able to fully describe the nucleation activity in the foaming process.

In this paper two kinds of polystyrene were used as the raw materials to prepare the foams with $scCO_2$ by the method of pressure-quench. The effects of various factors, such as the saturation time, saturation pressure, and foaming temperature on the cell structure were studied to determine the parameters influencing the foam structure. And the competition between cell growth and cell nucleation was used to explain foaming behaviors of PS.

2 Experimental Sections

2.1 Materials

General Purpose Polystyrene（GPPS，Polystyrol 158 K）particles and High Impact Polystyrene（HIPS, Polystyrol 476 L）particles were all kindly supplied by BASF-YPC Company Limited and used as received. CO_2(99.5%) and liquid nitrogen(99.9%) were purchased from Nanjing Gas Company of 55^{th} Institute and used as received.

2.2 Foam Preparation

Foams were prepared in a 100ml high pressure stainless steel vessel as shown in the previous paper [9].

2.3 Characterization

Differential scanning calorimetry (DSC, Mettler Toledo DSC 823E) was conducted on PS and PS foams. Weighted samples were heated up from 50 to 500℃ at a rate of 15℃/min under the nitrogen atmosphere environment.

The cell diameters, cell densities and volume expansion rates were analyzed by image pro plus software with the method of Zhu et al. [10].

3 Results and Discussion

3.1 Effect of Foaming Temperature

Fig. 1 shows the SEM micrographs of the fractured surfaces of GPPS and HIPS foams at different foaming temperatures for the saturation pressure of 20MPa and the saturation time of 6h. As shown in Fig. 1, at the foaming temperature of 90℃ and 100℃, the cells are highly expanded and cell walls are very thin. The foam at 100℃ exhibits larger cell size than that at 90℃.This result is in agreement with that of McCarthy [11]. But when the temperature is raised to 120℃, cells become small and cell walls become thick. This is mainly due to the gas escaping. As we known, the increase of the foaming temperature will decrease the melt viscosity, which benefits both cell coalescence and gas escaping. In GPPS foams, the gas escaping plays the dominant role, thus decreasing the cell diameter, and in HIPS foams, the cell coalescence plays the dominant role, thus increasing the cell diameter. The cell diameter of HIPS is much smaller than that of GPPS, because the melt viscosity of HIPS is higher than that of GPPS.

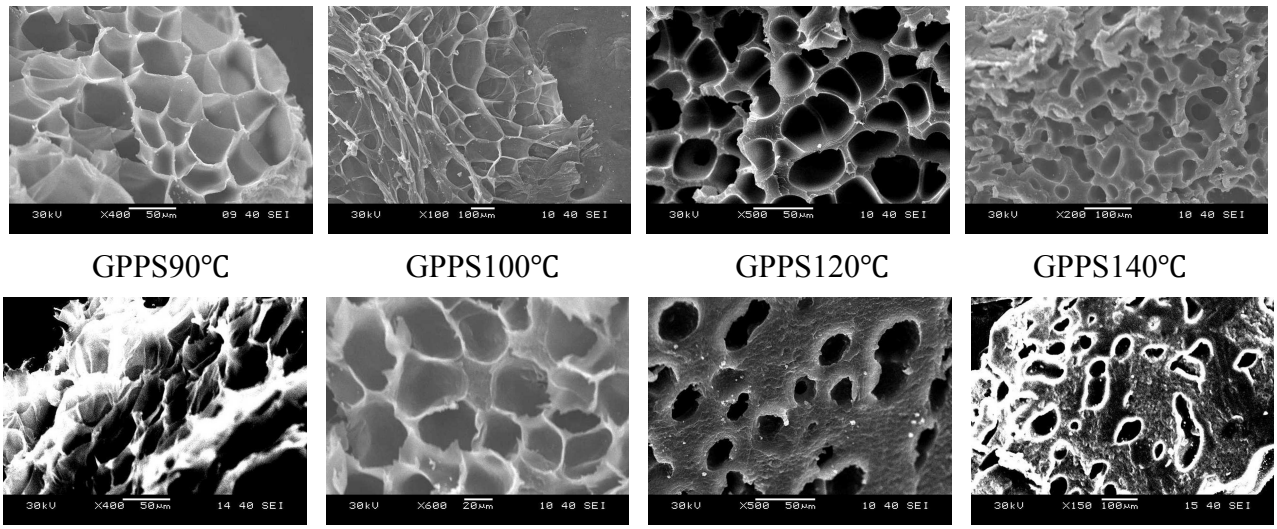

Fig. 1 SEM micrographs of GPPS and HIPS foams

3.2 Effect of Saturation Pressure

Table 1 shows cell parameters of GPPS and HIPS at different pressures. From Table 1, we can find that the cell diameter decreases and the cell density increases with the saturation pressure increasing. The increase of the saturation pressure can result in high solubility of CO_2, thus leading to high cell nucleation. More cells nucleate in the given volume, smaller cells generate. The increase of the foam density of GPPS and HIPS from 20MPa to 24MPa can be due to the slight escape of CO_2. The increase of the saturation pressure increases both the solubility and the plasticization, which can decrease the melt viscosity. The decrease of the melt viscosity can make CO_2 to escape more easily. But the cell nucleation is more sensitive to the saturation pressure and increases dramatically. Although the melt viscosity reduction can lead to the gas escaping, the plasticization effect is slight and can not influence the cell nucleation apparently.

Table 1 Cell diameters, cell densities and volume expansion rates of GPPS and HIPS at different saturation pressures

Samples	Saturation pressure [MPa]	Cell diameter [μm]	Foam density [g/cm^3]	Cell density [cells/cm^3]
GPPS	12	104.43	0.3638	1.10×10^6
	16	97.44	0.1449	1.78×10^6
	20	77.25	0.1059	3.73×10^6
	24	48.36	0.1943	1.38×10^7
HIPS	12	43.53	0.5561	1.09×10^7
	16	35.24	0.5805	1.95×10^7
	20	22.01	0.4603	1.16×10^8
	24	6.68	0.6177	2.64×10^9

3.3 Effect of Saturation Time

As shown in Fig. 2, as the saturation time increases, the cell density of GPPS foams decreases, while that of HIPS foams firstly increases and then decreases. So we can conclude that short saturation time can generate small cells, if the saturation time is prolonged too much, cells become large. There exists a suitable time, it is 2h for GPPS and 4h for HIPS. As we known, the heat and mass transfer is very slow in the polymer, long saturation time can make the polymer system to get mass and heat equilibrium, which can benefit the cell nucleation and cell growth. If the saturation time is suitable, it benefits the cell nucleation more than the cell growth, but if the saturation time is too long, it benefits the cell growth more than the cell nucleation.

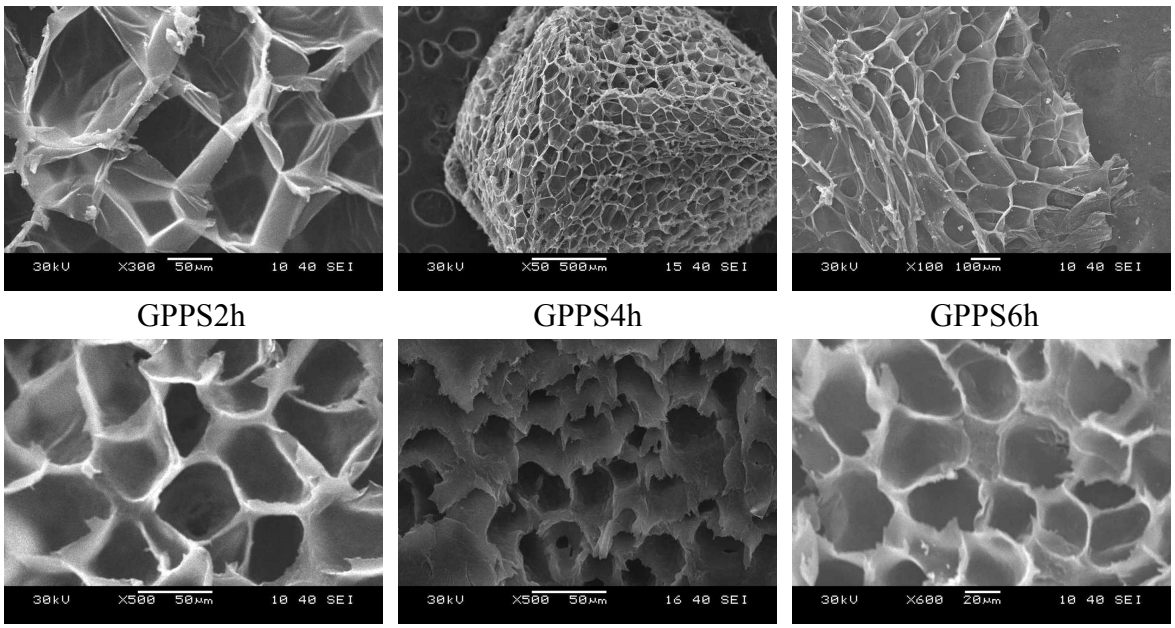

Fig. 2 SEM micrographs of GPPS and HIPS foams at different saturation time

3.4 DSC Characterization

Fig. 7 shows DSC curves of GPPS and HIPS at different foaming temperatures. In Fig. 7, GPPS means the original GPPS, GPPS 90℃ means GPPS foam which is foamed at the foaming temperature of 90℃ for the saturation pressure of 20MPa and the saturation time of 6h. From Fig. 7, it can be seen that the glass transition temperature (T_g) increases very slightly with the foaming temperature increasing. This means that foaming does not influence the T_g of PS apparently.

Interestingly, we find that the melting peak is very apparently at the foaming temperature of 90℃, but the peak of the original PS or PS foams at other foaming temperatures is small. The reason must be further investigated.

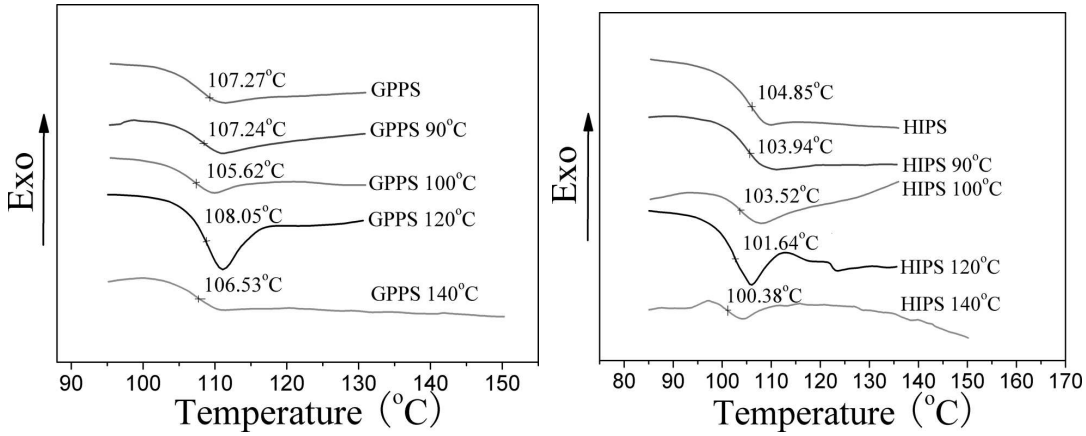

Fig. 3 DSC curves of original GPPS or HIPS and foams at different foaming temperatures

Summary

In this paper, we systematically investigate foaming behaviors of GPPS and HIPS. The cell diameter of GPPS is much larger than that of HIPS, because of the low melt viscosity of GPPS. Variations of cell diameter and cell density with the foaming temperature and saturation time are not the same as many previous researches, which is explained by the competition between cell growth and cell nucleation. Finally, the glass transition temperature almost remains constant with foaming condition variations.

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