Novel Dynamic Microcellular Polystyrene Processing in Supercritical CO_2

Chang-Yun Gao, Nan-Qiao Zhou, Xiang-Fang Peng
Key Laboratory of Polymer Processing Engineering, Ministry of Education,
National Engineering Research Center of Novel Equipment for Polymer Processing,
South China University of Technology, Guangzhou 510640, China.

Abstract

A novel dynamic foam processing simulator was constructed, which can form a steady shear flow and an oscillatory shear flow in the polymer melt. The oscillatory shear was superimposed perpendicular to the steady shear flow. The effects of saturation pressure and oscillatory shear on polystyrene cell morphology were investigated. The cell morphology was analyzed with a scanning electron microscope (SEM). The results show that the samples foamed with gaseous CO_2 have a small cell density. The cell density increases and cell size decreases significantly when processed with supercritical CO_2. The cell density increases and cell size decrease further with the increase of saturation pressure. The cells show an oval shape when processed under steady shear flow. While processed under superimposed oscillatory shear flow, a cell structure of nearly spherical cell shape was observed.

Key words: polystyrene foam, supercritical CO_2, mechanical vibration, oscillatory shear, orthogonal superposition

Introduction

Microcellular plastics have brought increasing interest in both academic and industry due to their unique properties and multiple applications. Environmental friendly supercritical fluids, primarily supercritical carbon dioxide (CO_2) and nitrogen (N_2), are used as foaming agents.

Recently, shear effect on foam processing and final cell morphology has brought increasing interests. Shear rate and shear stress influence not only the macroscopical shear flow but also the aggregated state of polymer melt at microcosmic scale, correspondingly, influence the polymer plastication, polymer/gas solution formation and cell nucleation. In order to produce microcellular foam with fine cell structure and specified properties, many efforts have been devoted to searching for efficient microcellular processing technologies and basic theories for foam processing. Chen *et al*. [1-3] developed a foaming simulator to investigate the gas absorption of filled /unfilled polymer system and the effect of shear stress on cell nucleation. Their results show that the cell density is increased significantly by introducing shear stress. A stretched nuclei model was used to explain the effect of shear stress on the cell nucleation.

Vibration techniques have been applied to polymer processing and show significant advantages. Ultrasonic, one of the melt vibration techniques, has been used in microcellular processing and gained some investigations[4-6]. The patented electromagnetic dynamic plasticating extruder [7] is another example utilizing vibration technique. The axial vibration with small amplitude of the screw applied to polymer processing has showed significant advantages, such as lower energy consumption, enhanced mixing degree, reduced viscosity, and improved mechanical properties of product. This technology has been used in polymer extrusion and injection molding, and some works have been done on the melt behaviors under this kind of vibration [8-14]. A novel dynamic processing technology for microcellular processing has been presented in the previous work [15], and a novel dynamic foam processing simulator utilizing mechanical vibration technology has been developed successfully. The purpose of this paper is to investigate the effects of saturation pressure and oscillatory shear on cell morphology using this novel dynamic foam processing simulator.

Experimental

Experimental setup

This experimental setup consists of four main parts (Figure 1): Supercritical fluid (SCF) delivery system, driving system, electromagnetic dynamic device, and foaming unit (similar to the setup used by Chen et al. [1-3]), as shown in Figure 2. The foaming unit basically consists of a foaming chamber and a rotor. The rotor can rotate circumferentially driven by an AC variable motor and a belt drive unit and vibrate axially driven by the electromagnetic dynamic device. The vibrating displacement of the rotor is monitored by a displacement transducer. The vibrating displacement is in the form of $u(t) = A\sin\omega t$, where *A* is the vibration amplitude, ω is the angular frequency that has a relation with the vibration frequency *f* as $\omega = 2\pi f$. The rotating and vibrating of the rotor can form a steady shear flow and an oscillatory shear flow in polymer melt, respectively. The oscillatory shear is superimposed perpendicular to the main steady shear flow, as shown in Figure 3. A 3/4″ release valve is used to get a pressure drop rate (dp/dt) up to 2×10^6Pa/s. The processing pressure of supercritical CO_2 can be regulated by the SCF delivery system up to 25MPa. In this study the pressure drop rate was controlled at about 2×10^6Pa/s for each condition.

The basic working principle of this setup is to form a single-phase polymer/gas solution under the shear (steady shear or combined shear) mixing of the rotor, followed by cell nucleation under thermodynamic instability induced by rapid pressure release.

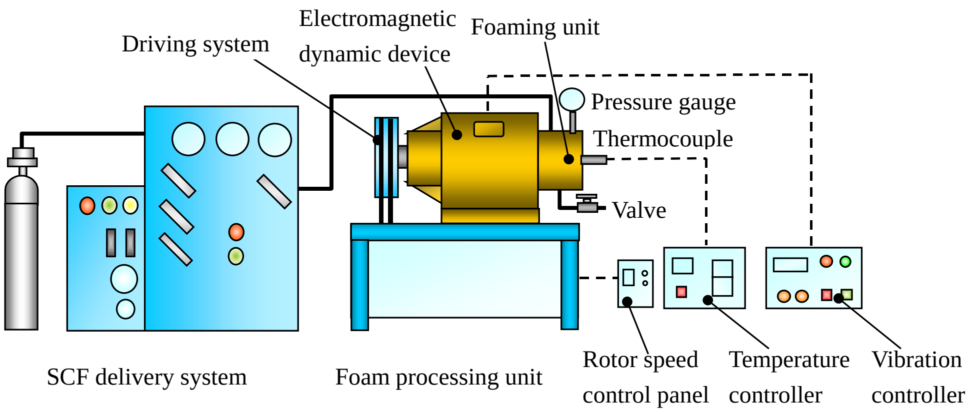


Figure 1 Schematic of experimental setup

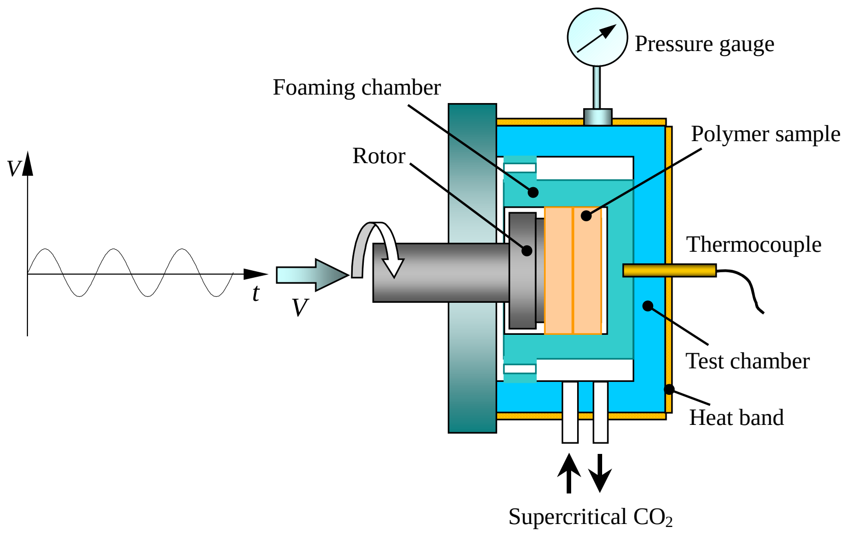


Figure 2 Schematic of foaming unit

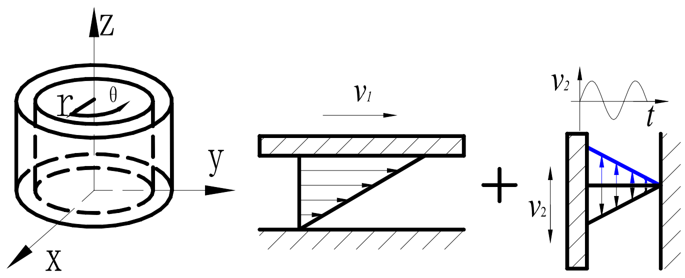


Figure 3 Schematic of the steady shear and oscillatory shear

Material

Material used in this study was pure polystyrene pellet (GPPS535), having a melt index of 1.73g/10min (190℃/5.0Kg), a bulk density of 1.05g/cm^3, and a glass transition temperature of 97℃. The PS pellet was compression molded with a curing press, obtaining cylinder polymer rings. The temperature of the curing press was set at 160℃, and the pressure was 7MPa. The blowing agent used in this study was environmental friendly CO_2, with a purity of 99.97%.

Analytical method

The PS cell morphology was analyzed by observing the cell morphology of foamed samples. The foam samples were fractured in liquid nitrogen and then coated with gold. A Phillip XL30 scanning electron microscope (SEM) was used to observe the cell morphology. The cell density was calculated with the same method used by Baldwin *et al.* [16] and Matuana *et al.*[17].

Procedure

Two sample rings were put into the foaming chamber to about 65% capacity of the foaming chamber. The foaming chamber was heated to foaming temperature was maintained at this temperature for 10 minutes to soften the material and reach heat equilibrium. When the temperature reached the specified temperature, the supercritical CO_2, with a constant pressure, was injected into the molten polymer forming a two-phase polymer/supercritical CO_2 mixture. When the pressure reached the experimental pressure, the rotor began to rotate. With the shear mixing of the rotor (steady shear or combined steady and oscillatory shear), the two-phase mixture is mixed, forming a single-phase polymer/ supercritical CO_2 solution. Then the rotor is stopped rotating and vibrating. The valve was opened quickly to release the pressure in the foaming chamber. The polymer/CO_2 solution nucleated under thermodynamic instability. Then the foamed sample was cooled to about 95℃, and then taken out from the foaming chamber. The cooling rate was kept the same in each experiment to maintain a similar condition for cell nucleation and bubble growth. The mixing time was calculated when the rotor began to rotate.

Results And Discussions

Effect of saturation pressure on cell morphology

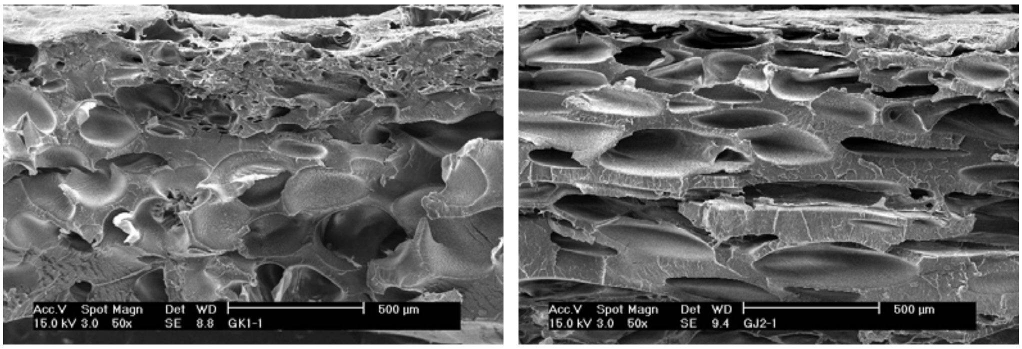
Figure 4(a) and (b) are the SEM micrographs of foam samples blown with gaseous CO_2. The saturation pressure is 6MPa and 6.5Mpa, respectively. Figure 5(a) and (b) are the SEM micrographs of foam samples blown with supercritical CO_2. The saturation pressure is 8MPa and 10Mpa, respectively. The processing temperature is 140℃ with rotor speed of 65r/min and mixing time of 5 minutes. For Figure 4 and Figure 5, the pressure drop rate was controlled at about 2MPa/s.

Figure 6 are the SEM micrographs at different saturation pressures with a constant temperature of 150℃, rotor speed of 65r/min, and mixing time of 5minutes. The saturation pressure is 8MPa, 9MPa, 10MPa, and 11MPa, respectively. The pressure drop rate was controlled at about 2MPa/s.

The effects of saturation pressure at 140℃ and 150℃ on cell density and average cell diameter are plotted in Figure 7 and Figure 8 respectively.

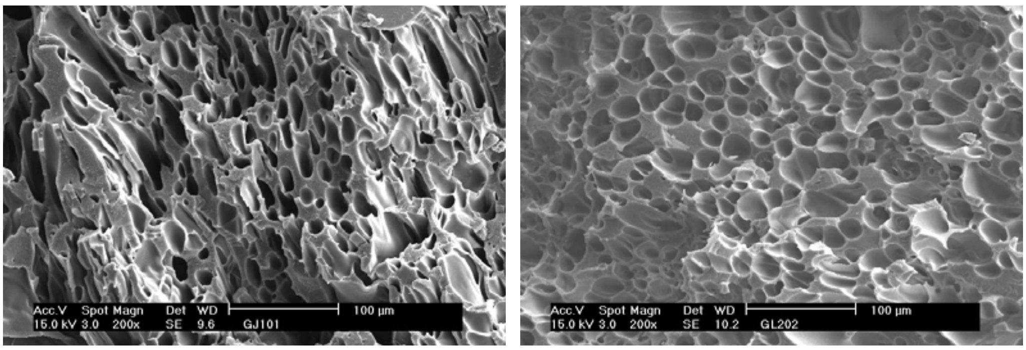
It is noted that the samples blown with gaseous CO_2 have a cell structure of small cell density and large cell size. While blown with supercritical CO_2, the cell density increases significantly, leading to a smaller cell size and uniform cell size distribution. The foam samples processed at 140℃ show a higher cell density and smaller cell size than those processed at 150℃. The cell density increase and cell size decrease with the increase of saturation pressure in both case. The cells at higher pressure show a narrow size distribution.

An abrupt change of cell density was observed when the CO_2 pressure was changed from 6.5MPa to 8MPa. Critical conditions met may be part of the explanation for the abrupt change in nucleation density. The critical state may however favorably affect the diffusion rate (more gas dissolved within a shorter period of time), but this need to be verified with adequate solubility/diffusivity measurements. It seems that supercritical CO_2 is benefit to nucleate a larger cell density.



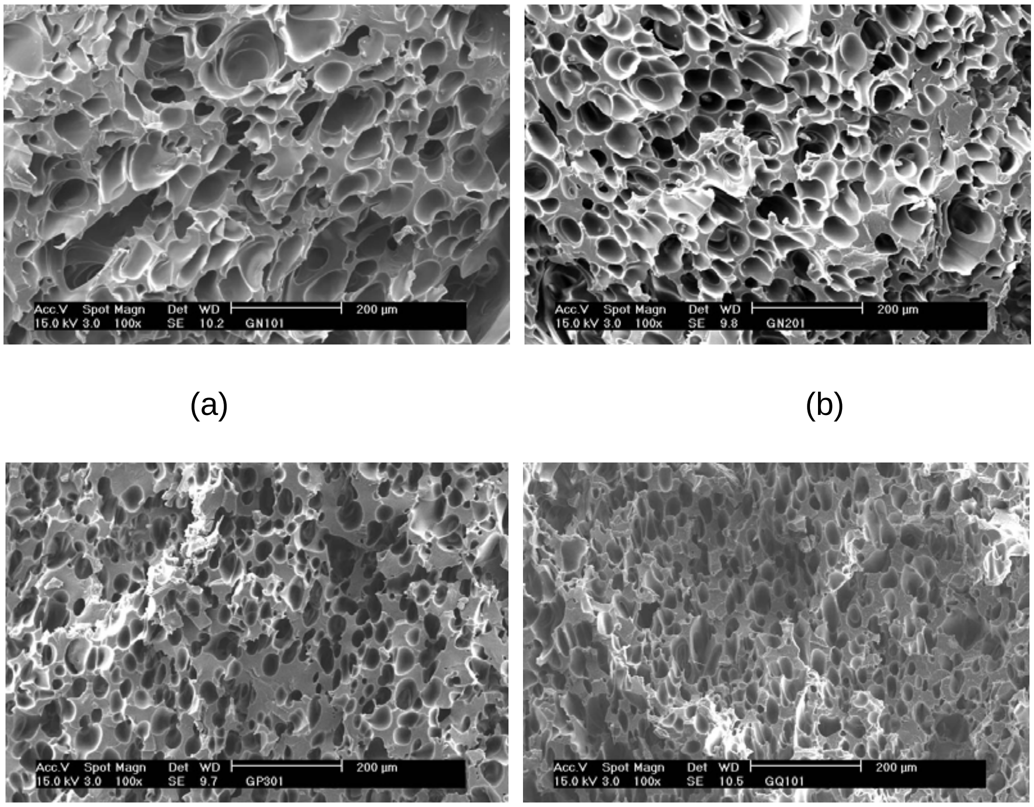
(a) (b)

Figure 4 Effects of gaseous CO_2 on cell morphology at 140℃: (a) 6MPa, (b) 6.5Mpa



(a) (b)

Figure 5 Effect of supercritical CO_2 on cell morphology at 140℃: (a) 8MPa, (b) 10Mpa



(a) (b)

(c) (d)

Figure 6 Effect of saturation pressure on cell morphology at 150℃: (a) 8MPa, (b) 9MPa, (c) 10MPa, and (d) 11Mpa

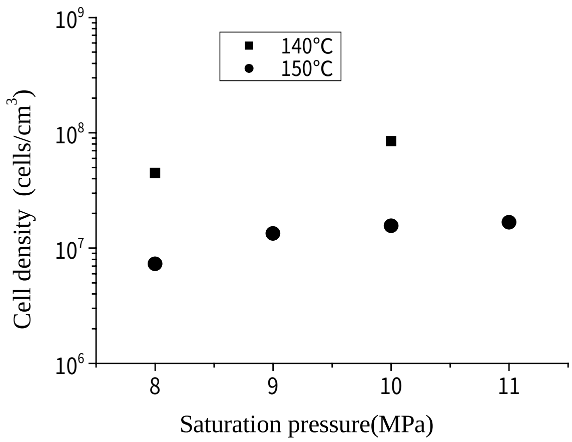


Figure 7 Effect of saturation pressure on cell density

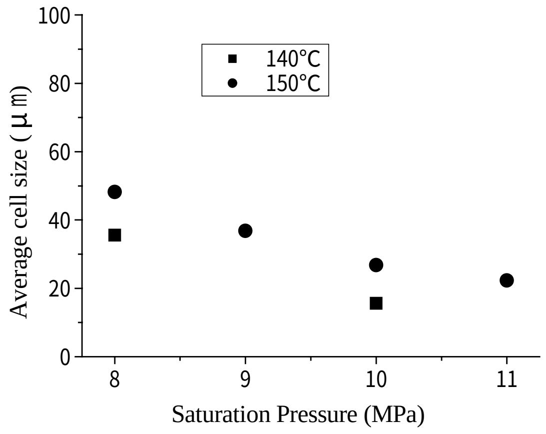


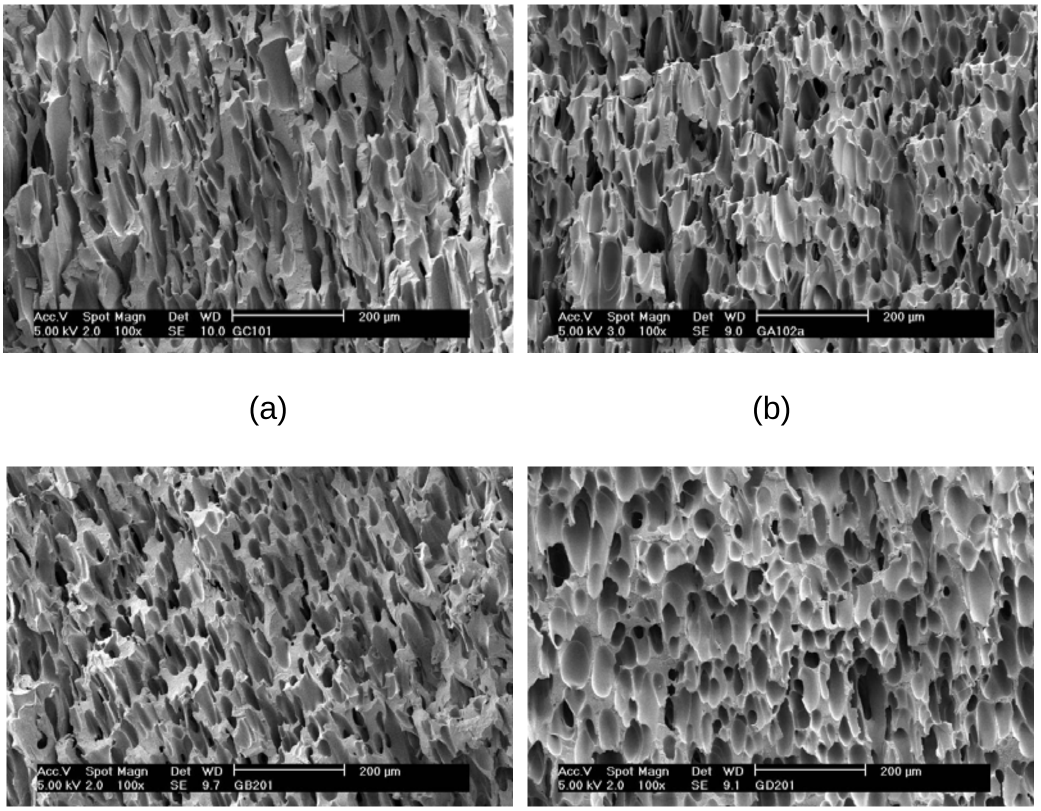
Figure 8 Effect of saturation pressure on average cell size

Effect of oscillatory shear on cell morphology

The SEM micrographs processed under rotor speed of 75r/min are shown in Figure 9. The fractured sections were parallel to the steady shear flow direction. Figure 9(a) is processed only under simple shear. Figure 9(b), (c) and (d) are processed under coupled steady and oscillatory shear. Figure 9(b) and (c) have the same vibration amplitude of 0.02mm, and the vibration frequencies are 10Hz and 20Hz, respectively. Figure 9(d) has the same vibration frequency with Figure 9(b), and the vibration amplitude is 0.04mm.

It was observed from the SEM micrographs that the cell shapes change with the vibration parameters. The cells show elongated shape when processed under steady shear. With the introduction of oscillatory shear this kind of elongation is not so remarkable as that processed under steady shear. It also can be seen that the contribution of oscillatory shear on PS cell morphology is different at different vibration parameters. In the case of 75r/min, when vibration frequency is 10Hz and amplitude is 0.04mm, the cells show the best cell shape. It seems to exist an optimum arrangement of rotor speed and vibration parameters for improved cell shape.

The final cell shape and cell distribution are the sign of molecular orientation and blowing agent distribution. The improved cell shape may due to the changed aggregated states of polymer melt and blowing agent distribution under combined shear flow of steady and oscillatory shear. Under orthogonal superposition of oscillatory shear, the molecular orientation is along the two shear flow directions and the distribution of blowing agent in the polymer melt becomes uniform. The orthogonal superposition of oscillatory shear is helpful to nucleate fine cell structures, and thus can improve final product properties.



(a) (b)

(c) (d)

Figure 9 Effect of superimposed oscillatory shear on PS cell morphology

Conclusions

A novel dynamic foam processing simulator has been developed. This setup can form a steady shear flow and an oscillatory shear flow by the axial vibration of rotor. The oscillatory shear was superimposed perpendicular to the steady shear flow in the foam processing.

The effects of saturation pressure and oscillatory shear on polystyrene cell morphology are investigated. An abrupt change of cell density was observed when CO_2 change from gaseous state to supercritical state due to the variation of conditions for polymer/CO_2 solution formation, cell nucleation and bubble growth. A fine cell structure was observed when processed at higher saturation pressure and lower temperature.

The shear flow has a significant influence on final cell morphology by influencing the molecular orientation and blowing agent distribution. When processed under combine shear, a cell structure of nearly spherical cell shape was observed. It is helpful to obtain fine cell structure with proper arranged rotor speeds and vibration parameters.

Acknowledgements

This work has been supported by the Research Foundation for the Doctoral Program of Higher Education under grant No. 20020561002, the Ministry of Education for the Key

Program of Scientific Research (Project No. (01) 224, 01138).

References

[1] Chen L, Sheth H, Kim R. Gas absorption with filled polymer systems. Polymer Engineering and Science. 2001, 41(6): 990-997.

[2] Chen L, Sheth H, Wang X. Effects of shear stress and pressure drop rate on microcellular foaming process. Journal of Cellular Plastics. 2001, 37(4): 353-363.

[3] Chen L, Wang X, Straff R, *et al.* Shear stress nucleation in microcellular foaming process. Polymer Engineering and Science. 2002, 42(6): 1151-1158.

[4] Park H, Youn J R. Study on reaction injection molding of polyurethane microcellular foam. Polymer Engineering and Science. 1995, 35(23): 1899-1906.

[5] Youn J R, Park H. Bubble growth in reaction injection molded parts foamed by ultrasonic excitation. Polymer Engineering and Science. 1999, 39(3): 457-468.

[6] Koo M S, Chung K, Youn J R. Reaction injection molding of polyurethane foam for improved thermal insulation. Polymer Engineering and Science. 2001, 41(7): 1177-1186.

[7] Qu J P, Method and equipment for electromagnetic dynamic plasticating extrusion of polymer materials, US Patent, No. 5,217,302, 1993.

[8] LIU Y J, QU J P, XU B P, *et al.* Studies on viscoelastic behaviors of polymer melt under the vibration force field. Polymer Materials Science and Engineering. 2004, 20(1): 18-21.

[9] Qu J P. Study on the Pulsating Extrusion Characteristics of Polymer Melt through Round Sectioned Die. Polymer-Plastics Technology and Engineering. 2002, 41(1): 115-132.

[10] Qu J, He G, He H, *et al.* Effect of the vibration shear flow field in capillary dynamic rheometer on the crystallization behavior of polypropylene. European Polymer Journal. 2004, 40(8): 1849-1855.

[11] Qu J P, Xu B P, Jin G, *et al.* Performance of filled polymer systems under novel dynamic extrusion processing conditions. Plastics, Rubber and Composites. 2002, 31(10): 432-435.

[12] Qu J P, Zhang J. Transient network structural model of polymer melts for extrusion flow in vibration force field. Journal of South China Universit y of Technology (Natural Science Edition). 2002, 30(11): 21-26.

[13] Liu Y J, Qu J P, Fan S H, *et al.* Relationship between shear stress and shear strain of polymer melt under vibrating force field. Plastics, Rubber and Composites. 2004, 33(2-3): 120-124.

[14] Qu J, Peng X, Zhou N. Research on elastic behaviors of LDPE melt during capillary dynamic extrusion. Journal of South China University of Technology (Natural Science). 1998, 26(11): 1-7.

[15] Gao C, Zhou N, Peng X, *et al.* Effect of vibration shear on polystyrene cell morphology. ANTEC 2005 - Annual Technical Conference Proceedings, May 1-5 2005, Boston, Massachusetts, United States. Society of Plastics Engineers, 2005: 2691-2695.

[16] Baldwin D F, Park C B, Suh N P. Microcellular processing study of poly(ethylene terephthalate) in the amorphous and semicrystalline states. Part I: Microcell nucleation. Polymer Engineering and Science. 1996, 36(11): 1437-1445.

[17] Matuana L M, Park C B, Balatinecz J J. Processing and cell morphology relationships for microcellular foamed PVC/wood-fiber composites. Polymer Engineering and Science. 1997, 37(7): 1137-1147.