

# A New Technique for Preparing Polyethylene/Polystyrene Blends with Gradient Structure

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**ABSTRACT:** In this study, polyethylene (PE)/polystyrene (PS) polymeric gradient material with spatially gradient structure was prepared continuously by a new technique through coextrusion–gradient distribution–two-dimensional mixing with conventional polymeric material processing facilities. The processing line from coextrusion, gradient distribution to two-dimensional mixing was fulfilled by two extruders, gradient distribution unit, and two-dimensional mixing units, respectively. The gradient distribution unit and two-dimensional mixing units were designed separately in our group. The gradient variation of composition along the sample thickness direction was studied by differential scanning calorimetry (DSC) and scanning electron

microscopy (SEM). DSC results indicated that a gradient variation of the content of PE was formed along the sample thickness direction. SEM results showed the direct evolution of morphology of each specimen along the sample thickness direction. The experimental results demonstrated that the processing method with coextrusion–gradient distribution–two-dimensional mixing can be served as a new way to produce polymer blends with spatially gradient structure and worth to be further investigated. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2737–2743, 2007

**Key words:** polymer gradient material; polyethylene; polystyrene; processing; structure

## INTRODUCTION

Different from homogeneous materials, which have no spatial variation of properties and can be prepared and analyzed by many common techniques, functionally gradient material (FGM) is a new type of composite whose microelements (including composition and structure) change spatially to optimize the gradient properties for a specific application. Since a new-type of ceramic/metal composite as super heat-resistant materials for aerospace application was successfully implemented, FGM has attracted more and more scientists' attention.<sup>1–3</sup> On one hand, various preparing methods have been reported, including powder processing, thermal spraying, chemical vapor deposition, physical vapor deposition, combustion synthesis, diffusion treatment, and so on.<sup>4–8</sup> On the other hand, their applications have extended to various kinds of areas (nuclear energy, electron, optics, electromagnetism, chemistry, and biological medicine<sup>9,10</sup>). Oguma et al.

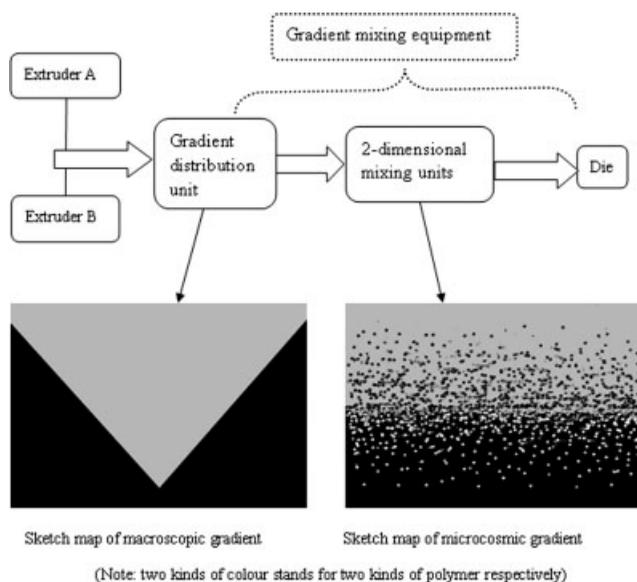
successfully prepared functionally gradient polymer electrolyte by plasma polymerization and found that the ionic conductivity increased from surface to bulk of the plasma polymer.<sup>11</sup> As for the types of FGM, they can usually be made from metal/ceramic, metal/alloy, nonmetal/nonmetal, nonmetal/ceramic, and ceramic/ceramic. However, only a few studies focused on polymeric gradient materials (PGM). Since 1990s, several research groups have been making their effort on preparation methods and structural characterization of PGM. These methods include gradient temperature, fibers stacked gradually up in a matrix, centrifugal force field, photopolymerization, diffusing copolymerization, and so on.<sup>12–26</sup> Reported by Liu et al., gradient refractive index polymer optical rods were successfully fabricated by swollen-gel polymerization technique.<sup>12</sup> Wen et al. has prepared the PP/talc gradient materials by gradually varying the component ratio of PP and talcum powder during extrusion process and found that the mechanical performance and thermal behavior of PP-talc composites gradually varied along the radius direction.<sup>13</sup> They also studied the preparation method of PP/PA6 gradient materials and found that the weight ratio of PP and PA6 changed gradually with progress of processing.<sup>14</sup> However, most of the above-mentioned preparing methods are complicated, hard to handle, and could not prepare PGM continuously by using traditional polymer material processing facilities. Furthermore,

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**Figure 1** Flow chart of processing route in the experiment.

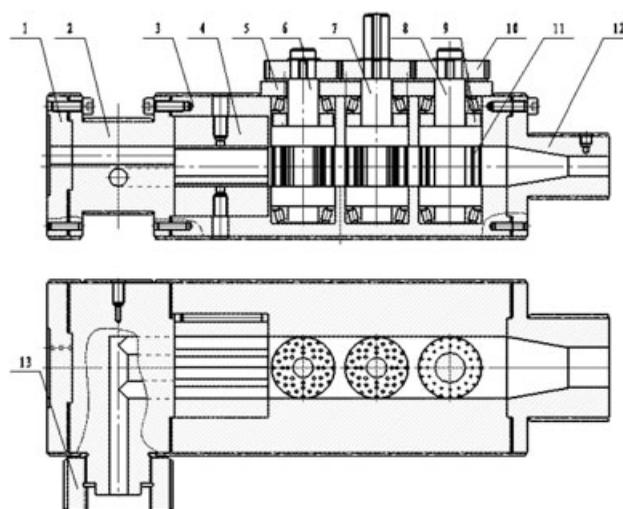
the PGM prepared by those methods often has small size and simple feature, and it is hard to prepare the PGM with large size and complicated feature. Because of the inherent shortcomings, it is far from industrial application.

In this work, we use a new processing method to prepare PGM continuously through coextrusion–gradient distribution–two-dimensional mixing with conventional polymeric material processing facilities. The facilities of this method include two extruders, gradient distribution unit, and two-dimensional mixing units. The aim of this study is to use this new way to produce polyethylene (PE)/polystyrene (PS) PGM continuously. A good gradient variation of component along the sample thickness direction has been obtained. The experiment results indicate that it is possible to produce PE/PS PGM continuously by using the processing method with coextrusion–gradient distribution–two-dimensional mixing. This method is worth to be further investigated and extended to other polymer systems.

## EXPERIMENTAL

### Design of processing method

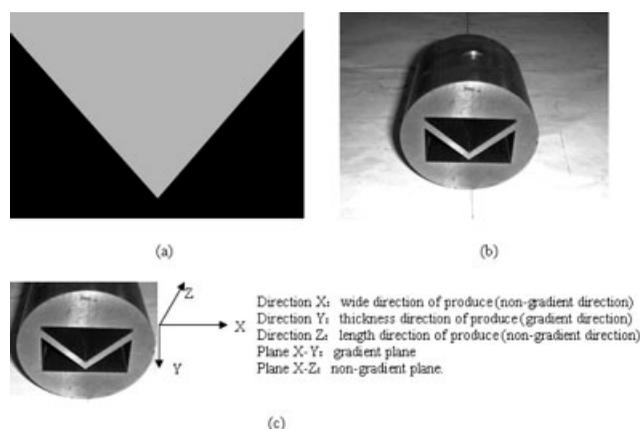
A new processing method to prepare PGM continuously has been brought up in our group. The flow chart of the processing route is schematically shown in Figure 1. Firstly, two kinds of polymer are extruded by two extruders, (used as a coextrude-system) respectively. Then, the two polymer melts are forced to form macroscopic gradient blend through a gradient distribution unit and followed by a two-dimensional mixing units; finally, the PGM is



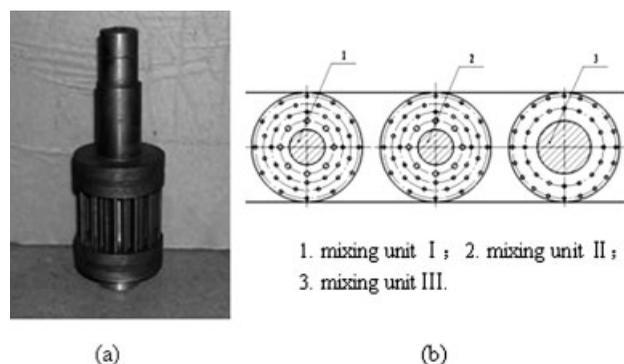
**Figure 2** Design of the gradient mixing equipment, (1) joint of twin-screw extruder; (2) transition unit; (3) mixing room; (4) gradient distribution unit; (5) board for pressing; (6–8) two-dimensional mixing units; (9) block for pressing; (10) gear wheel; (11) mixing rod; (12) die; (13) joint of single-screw extruder.

obtained through the die and solidified via cooling. The size of the die is 15 mm in thickness and 60 mm in width.

Figure 2 shows the design of gradient mixing equipment. Gradient distribution unit is the core of the experimental equipment, which functions to make the melt from the two extruders form a macroscopic gradient along sample thickness direction. Figure 3(a) shows an illustration of macroscopic gradient, and the photograph of corresponding gradient distribution unit is shown in Figure 3(b). It is a rectangle channel with a “V” clapboard, which separates the melt from two extruders. The temperature of the gradient distribution unit is controlled by the outside heater, which keeps the polymer in the molten state.



**Figure 3** (a) An illustration of the macroscopic gradient; (b) Photograph of the gradient distribution unit; (c) the defined directions of the gradient distribution unit.



**Figure 4** (a) Photograph of a mixing unit. (b) Top-cut-away plan of mixing units.

To explain the principle of operation more clearly, we define three directions and two planes for the gradient distribution unit, as shown in Figure 3(c). After the polymer melt passing through the upper gradient distribution unit, it will be mixed in two dimensions through the two-dimensional mixing units, and then a microcosmic gradient in the thickness direction is achieved.

The two-dimensional mixing unit is shown in Figure 4(a). Its function is to mix the two polymer melts homogeneously in each layer to form the microcosmic gradient. A key point in our design is to keep the two kinds of component mixed in the nongradient direction but not move them in the gradient direction. This is theoretically feasible because the viscosity of polymer is very high and the polymeric melt will keep the laminar flow in each layer and will not form the onflow in the die when being extruded. The last point to consider is how to bring the mixing in two-dimensional directions (each layer in flow direction). One must bring enough shearing and stretching stresses to achieve the dispersing and distributing mixing in each layer. This can be achieved by a two-dimensional mixing unit.

Three mixing units are used to achieve the two-dimensional mixing. As shown in Figure 4(b), there are similar mixing rods distributing around circumference of every mixing unit. The function of the mixing rods is to bring about shearing and stretching stress to achieve the dispersing and distributing mixing. When the mixing units are rotating, the mixing rods will make revolution in the mixing room, and so they can bring the polymeric melt strong shearing and stretching stress, which provides a compulsive convection and thus a good mixing.

The rotation of two-dimensional mixing units is implemented by the circumrotate drive system, which include an electromotor, a shelf for fixing the electromotor, and a series of gear wheels. A picture of circumrotate drive system is shown in Figure 5.

## Materials

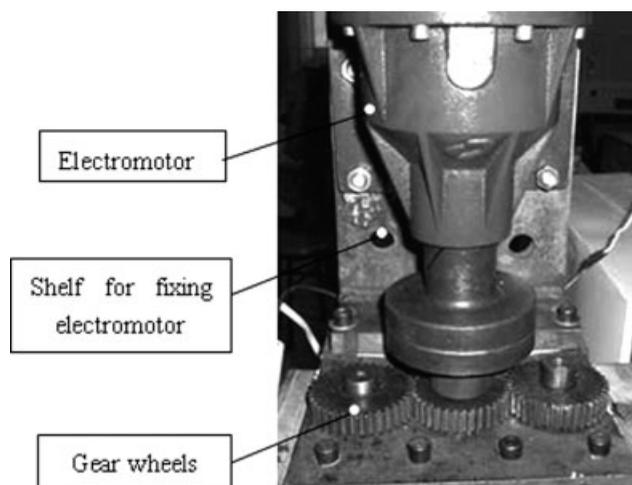
Commercial PE (5000S,  $M_w = 3.3 \times 10^5$  g/mol) used in this study were manufactured by Lanchow Petrochemical Inc, with a melt flow rate of 0.95 g/10 min (200°C, 2.16 kg). PS (666D,  $M_w = 2.5 \times 10^5$  g/mol) were provided by Beijing Yanshan petrochemical Co. Ltd, with a melt flow rate of 1.2 g/10 min (200°C and 2.16 kg).

## Sample preparation

PE was extruded by a twin-screw extruder with a screw diameter of 18 mm and a length to diameter ratio of 20, and PS was extruded by a single-screw extruder with a screw diameter of 30 mm and a length to diameter ratio of 25. To see whether the gradient has formed or not in this process with naked eye, a little Color Master Batch was added into twin-screw extruder with PE. The parameters of the experiment are listed in Table I. The processing route for preparing PE/PS PGM is shown in Figure 6.

## Characterization

A photograph of the prepared PE/PS PGM by our new technique is shown in Figure 7. One can observe the sample positions cut for characterization along sample thickness direction from this figure. The thickness of the PGM is about 15 mm. As shown in Figure 7, the selected five positions were 0.1*t*, 0.3*t*, 0.5*t*, 0.7*t*, 0.9*t* along the thickness direction, where *t* is the thickness of the sample, and they are signed as a, b, c, d, e, respectively. Such five specimens from the corresponding positions were used for differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) observation.



**Figure 5** Photograph of the circumrotate drive system.

TABLE I  
Processing Parameters

Equipment	Extrude temperature (°C)				Feeding speed (rpm)	Rotating speed (rpm)
	Segment 1	Segment 2	Segment 3	Segment 4		
Twin-screw extruder	140	170	180	200	95	120
Single-screw extruder	140	180	200	–	–	35
Gradient mixing equipment	200	200	200	–	–	–

### Differential scanning calorimetry

As for PE/PS blend, PS is a typical amorphous polymer and its  $T_g$  ranges from 90 to 100°C, whereas PE is a typical crystalline polymer and its melting point is about 130°C. So we can qualitatively analyze the variation of composition by observing the change of endothermic peak at the two characteristic temperatures. In this study, to determine the gradient variation of composition along sample thickness direction, endothermic peak at each selected position was measured by a Perkin–Elmer pyris-1 DSC with nitrogen as purge gas. The specimens (about 5 mg) were heated to 160°C at a heating rate of 10°C/min. Pyrograms from 20 to 160°C were recorded.

### SEM observations

The dispersion and distribution of the components in PE/PS composites were examined under an acceleration voltage of 20 kv with a JEOL JSM-5900 LV for SEM experiment. Before being examined, the specimens of PE/PS composites were cryogenically fractured in liquid nitrogen and etched by methylene chloride.

## RESULTS

### Gradient variation of composition

The gradient variation of composition of the PE/PS specimen was investigated with DSC. The endother-

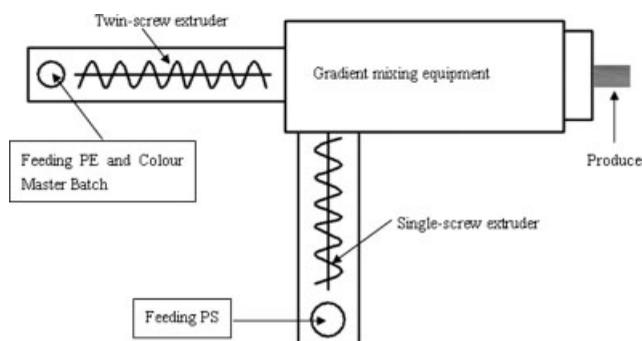


Figure 6 The schematic diagram of the processing route for preparing PE/PS PGM.

mic peak of PS was not shown because it is too small. The melting traces of the five PE/PS gradient specimens at a heating rate of 10 K/min are shown in Figure 8. It can be seen from this figure that the melting peak of all the five PE/PS gradient specimens occurred at about 130°C, which is the melting temperature of PE. It is well known that the value of the melting peak area is directly proportional to the crystallinity in a homopolymer material. Therefore, the value of the melting peak area can be used to evaluate the content of PE in PE/PS blends. From this figure, we can see that the peaks become weaker from specimens a–e, suggesting that the content of PE in the blend decreased gradually along the thickness direction. Figure 9 shows the variation of the melting enthalpy in PE/PS PGM along sample thickness direction. One can see that the melting enthalpy gradually decreased with the increase of sample thickness, which indicates that the component gradient has formed in PE/PS blends. It is to be noted that the slope of Figure 9 represents the changing rate of melting enthalpy of the blend. It can be clearly seen that this rate slightly fluctuates along the thickness direction, which indicates that the changing rate of PE content slightly fluctuates along the thickness direction. In summary, the results indicate that PE/PS gradient material were successfully prepared.

### Evolution of morphology

We all know that the blend of PE/PS is immiscible because its structure is remarkably different. Accord-

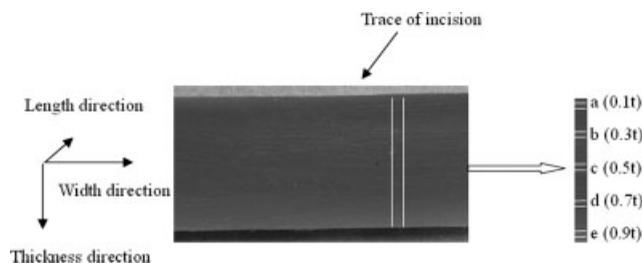
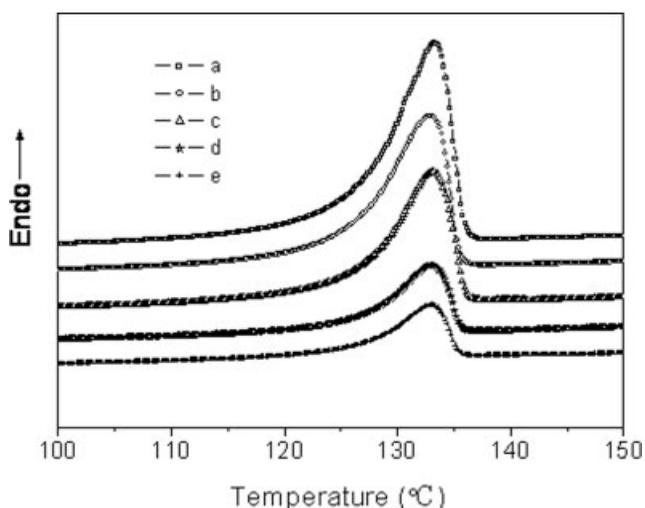


Figure 7 Photograph of PE/PS polymeric gradient material sample. (a–e) represent the selected five positions along the thickness direction; 0.1t, 0.3t, 0.5t, 0.7t, 0.9t is the relative height taken the whole sample height as  $t$ .



**Figure 8** Melting traces of various specimens at a heating rate of 10 K/min. (a–e) represent the five samples selected in different positions along the thickness direction as shown in Figure 7.

ing to traditional blend theory, a multiphase structure is expected to exist in the PE/PS blend. This morphological feature of the PE/PS gradient sample was examined by SEM. Typical SEM micrographs of the PE/PS gradient materials sampled at different positions along the thickness direction are shown in Figure 10. It should be mentioned that all the specimens were fractured at liquid nitrogen temperature, and PS was etched by methylene chloride before being examined by SEM. Therefore, many cavities were left as can be seen in this figure. These cavities represent PS particles. From Figure 10(a), one can see that the PS particles are of small size and disperse in PE matrix evenly, resulting in a typical sea-island morphology. It can be documented that the content of PS is at a low level for this sample. Compared to Figure 10(a), it can be clearly seen that both the size and quantity of the PS particles obviously increased in Figure 10(b), while the morphology feature did not change. This indicated that the content of PS became higher. However, Figure 10(c) shows a remarkable morphological transition from particle to column, suggesting the obvious increase of PS content. From Figure 10(d), one can observe that the bicontinuous morphology was formed, resulting in a phenomenon of phase inversion, which indicated that a further increase of PS content occurred. Figure 10(e) shows an abnormal morphology feature of the PE/PS blend. It can be seen that the size of cavities is very large, suggesting that almost no PE particles dispersed in PS matrix. It can be documented that the content of PS is at a very high level.

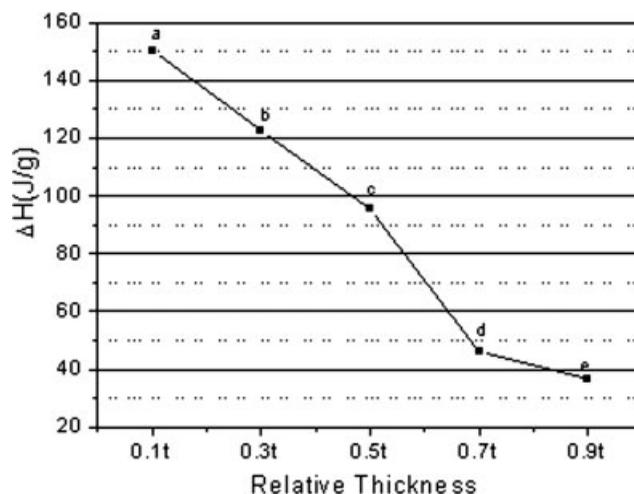
SEM results indicated that the local morphology feature of PE/PS blends prepared in this work is similar to those of the traditional blend, whereas the

whole structure is remarkably different because the morphology of each specimen varies gradually along the sample thickness direction. The content of PS in PE/PS blends increased gradually along the sample thickness direction. This is in agreement with the DSC results, which indicated that the content of PE in PE/PS blends decreased gradually along the sample thickness direction. In a word, the spatially component gradient structure has indeed formed in PE/PS blends by using our designed processing method.

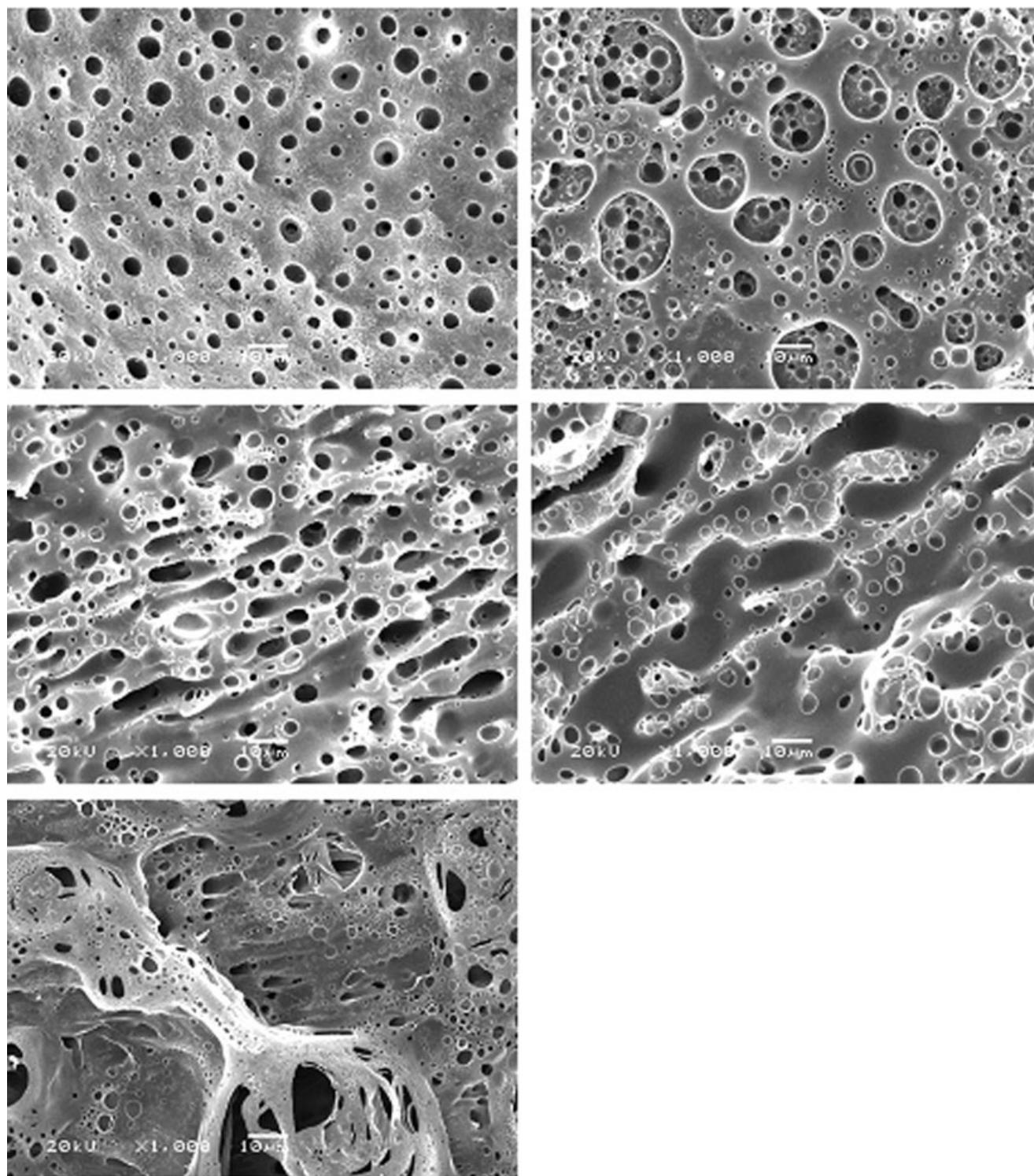
## DISCUSSION

On investigating the variation of composition of the PE/PS PGM, we have found from the DSC results that the content changing rate of PE fluctuates along the thickness direction. Considering the limit of experimental equipment and the different intrinsic properties of PE and PS, there may be several reasons. Firstly, two different extruders were used as the coextrude system, which would lead to the variance of extruding speed. Thus, it was difficult to avoid the polymer moving in the gradient direction. Secondly, the rotation of mixing units may be brought about by elastic turbulent flow of the melt. Therefore, the component of the PE/PS blends may become disordered in the gradient direction. Thirdly, because of the different melt viscosity of PE and PS in the different nongradient plane, the low viscosity melt (PS) may coat the high viscosity melt (PE).

As a result of the limit of experimental equipment, the PE/PS PGM formed by the new technique is not ideal. Some amelioration has to be made to improve



**Figure 9** The variation of melting enthalpy of PE/PS PGM along thickness direction. (a–e) represent the selected five different positions along the thickness direction as shown in Figure 7.



**Figure 10** SEM micrographs of various specimens sampled at different position in thickness direction. (a)  $0.1t$ , (b)  $0.3t$ , (c)  $0.5t$ , (d)  $0.7t$ , (e)  $0.9t$  represent the five samples selected in different positions along the thickness direction as shown in Figure 7.

the gradient structure of the PGM. On one hand, the design of the gradient distribution unit, two-dimensional mixing units, and die should be optimized to keep the gradient structure during the mixing and

molding, as the gradient mixing equipment is the key to form the gradient structure in this study. On the other hand, the same extruders should be used to assure the consistent extruding speed and reduce

the fluctuation of the content changing rate of PE because whether the speed of coextrude is matched or not is important. Furthermore, it would be better to carry out sight-study of the mixing and establish physical and mathematical model by computer simulation technique to depict the mixing in the gradient mixing equipment.

### CONCLUSIONS

In this study, PE/PS PGM was prepared continuously by a new technique through coextrusion–gradient distribution–two-dimensional mixing with conventional polymeric material processing facilities. The gradient variation of composition along the sample thickness direction was studied by DSC and SEM. DSC results indicated that a gradient variation of the content of PE was formed along the sample thickness direction. SEM result showed the direct evolution of morphology of each specimen along the sample thickness direction and indicated that the content of PS in PE/PS blend increased gradually along the sample thickness direction. All experimental results indicated that the processing method with coextrusion–gradient distribution–two-dimensional mixing can be served as a new way to successfully prepare PE/PS blends with spatially gradient structure and worth to be further investigated.

### References

1. Markworth, A. J.; Ramesh, K. S.; Parks, W. P. *Mater Sci* 1995, 30, 2183.
2. Hui, P. M.; Zhang, X.; Markworth, A. J.; Stroud, D. *Mater Sci* 1999, 34, 5497.
3. In Abstracts of the Third International Symposium on Structural and Functional Gradient Materials. Ilschner, B., Cherradi, N., Eds.; Lausanne: Switzerland, 1994.
4. Kawasaki, A.; Watanabe, R. *Eng Fract Mech* 2002, 69, 1713.
5. Government Industrial Research Institute, Tohoku. *Japan Metallurgy* 1990, 57, 302.
6. Zavaliangos, A. *Met Powder Rep* 1999, 54, 37.
7. Kieback, B.; Neubrand, A.; Riedel, H. *Mater Sci Eng A* 2003, 362, 81.
8. Liu, G. R.; Han, X.; Lam, K. Y. *Compos Mater* 2001, 35, 954.
9. Kaysser, W. A. *Mater Sci Forum* 1999, 1068, 308.
10. Uemura, S. *Mater Sci Forum* 2003, 1, 423.
11. Oguma, Z.; Abe, T.; Nakamura, S. *Solid State Ionics* 1999, 121, 289.
12. Liu, J. H.; Liu, H. T.; Cheng, Y. B. *Polymer* 1998, 39, 5549.
13. Wu, G.; Wen, B. Y.; Hou, S. H. *Polym Int* 2004, 53, 749.
14. Wen, B. Y.; Li, Q. C.; Hou, S. H.; Wu, G. *J Appl Polym Sci* 2004, 91, 2491.
15. Funabashi, M. *Trans Jpn Soc Mech Eng*, 1997, 63, 1022.
16. Funabashi, M. *Compos A* 1997, 28, 731.
17. Murayama, S.; Kuroda, S.; Osawa, Z. *Polymer* 1993, 34, 3893.
18. Ohtsuka, Y.; Sugano, T. *Appl Opt* 1983, 22, 413.
19. Koike, Y. *Appl Opt* 1985, 34, 4821.
20. Agari, Y.; Shimada, M.; Ueda, A.; Nagai, S. *Macromol Chem Phys* 1996, 197, 2017.
21. Kano, Y.; Akiyama, S.; Sano, H.; Yui, H. *Polymer* 1997, 29, 158.
22. Lambros, J.; Santare, M. H.; Li, H. *Exp Mech* 1999, 39, 184.
23. Tran, C. Q.; Okanaka, J. *Polym Eng Sci* 1999, 39, 365.
24. Xie, X. M.; Matsuoka, M.; Takemura, K. *Polymer* 1992, 33, 1996.
25. Jang, J.; Han, S. *Compos A* 1999, 30, 1045.
26. Huang, Z. M.; Wang, Q. A.; Ramakrishna, S. *Polym Polym Compos* 2002, 10, 307.