

FRACTIONATED CRYSTALLIZATION OF HDPE IN PS/POE/HDPE/SBS BLENDS*

Ming-ming Ding, Xiao-ting Fu, Jing Cao, Qin Zhang, Chang-yue Yang and Qiang Fu**

Department of Polymer Science & Engineering, Sichuan University, State Key Laboratory of Polymer Materials
Engineering, Chengdu 610065, China

Abstract The fractionated crystallization behavior of the minor dispersed HDPE phase in PS/POE/HDPE/SBS quaternary blends was investigated by differential scanning calorimetry (DSC). Interestingly, we found that the fractionated crystallization behavior of HDPE was molecular weight dependent. At a fixed composition, HDPE with lower molecular weight showed more obvious fractionated crystallization behavior than HDPE with higher molecular weight. This was ascribed to a finer dispersion of HDPE with lower molecular weight, as evidenced by SEM observations. The fractionated crystallization behavior of HDPE in the blends became less obvious with increasing of its content, due to a change of phase morphology from droplet to co-continuous structure. Correspondingly, a change of tensile toughness of the blends from brittle to ductile mode was observed.

Keywords: Fractionated crystallization; HDPE; Molecular weight dependent.

INTRODUCTION

Nucleation is a primary step in polymer crystallization. The nucleation process could be heterogeneous nucleation, homogeneous nucleation or self-nucleation. Polymer crystallization is usually initiated *via* heterogeneous nucleation owing to the presence of heterogeneities while homogeneous nucleation is rarely observed. However, in immiscible polymer blends, if the minor crystalline component is well dispersed as numerous particles, the number of which is greater than that of active heterogeneities, a series of crystallization temperature peaks appear at different degrees of supercooling, often ending with a crystallization peak at the homogeneous nucleation temperature $T_{c,hom}$. The presence of more than one crystallization temperature peaks is known as fractionated crystallization^[1–6]. The fractionated crystallization is usually observed in dispersed domains of crystallizable polymers with lower molecular weight^[7]. The fractionated crystallization could be explained as successive nucleating activities of different entities during cooling, as described by Freach *et al.*^[8]. Not all seeds are active at the same temperature, so generally crystallization starts as nucleated by the most active seeds, while it proceeds as function of large supercooling on crystallites already grown^[9]. The droplets of different size which contain heterogeneities of different activities will crystallize at different degrees of supercooling^[10]. The larger droplets that contain active heterogeneities will crystallize at higher temperature or smaller supercoolings. The smallest droplets that do not contain any heterogeneities will only be nucleated at the largest supercooling, since a greater supercooling is usually needed in order to generate homogeneous nucleus^[11–14]. Müller *et al.* recently demonstrated that the lack of active nucleus in the confined block copolymer domains plays a major role in the occurrence of homogeneous nucleation^[15]. A similar phenomenon was also observed in polypropylene/poly(ϵ -caprolactone) blends where the minor PP phase crystallized in a fractionated

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**Corresponding author: Qiang Fu (傅强), E-mail: qiangfu@scu.edu.cn

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way, by applying a self-nucleation procedure. This was believed to be due to the lack of highly active heterogeneities within the confined PP domains^[16].

Recently the fractionated crystallization behavior of polyethylene in several systems has been reported^[17–22]. The crystallization of polystyrene (PS)/high-density polyethylene (HDPE)^[23], polystyrene/low-density polyethylene (LDPE)^[24, 25], polystyrene/linear low-density polyethylene (LLDPE)^[26] blends were investigated in which PS was always the matrix component.

Polystyrene is one of the widely used plastics with good properties, however, the large amount of disposable polystyrene and expanded polystyrene plastic wastes produced nowadays makes imperative the search for recycling them since they are not biodegradable^[27–29]. The recycled polystyrene (rPS) has the unsatisfactory mechanical properties of low impact strength due to degradation during processing and service. Blending rubber with rPS is the most efficient way to improve the impact toughness and extend its application range so far^[30–33]. In order to enhance the toughness of recycled PS for TV backset, PS/POE/HDPE/SBS blends were designed and an obvious increase of tensile toughness of recycled PS has been achieved^[34]. Since the crystallization kinetics and morphology of the minor dispersed HDPE phase also played a role in determining the toughness of the blends, in this work, the crystallization behavior of HDPE in the blends was investigated as function of its molecular weight and content. The fractionated crystallization behavior of the minor dispersed HDPE phase has been found where three crystallization peaks were observed during cooling. Interestingly, the fractionated crystallization behavior of HDPE in the blends depended on its molecular weight and content.

EXPERIMENTAL

Materials

The materials used for the preparation of PS/POE/HDPE/SBS blends were listed in Table 1. Recycled polystyrene (rPS), ethylene-octylene copolymer thermoplastic elastomer (POE), high-density polyethylene (HDPE) and styrene-butadiene-styrene copolymer (SBS) used in our study were commercially available. To investigate the effect of molecular weight on the dispersion and subsequent crystallization of HDPE in the blends, HDPEs with different molecular weight [different melt flow index (MFI) (g/10 min) ranging from 0.05 to 20] were employed.

Table 1. Materials

Trade marked	Supplier	Characteristics	M_n
rPS	Changxin corp, MianYang, China	MFI: 25.8 g/10 min (200°C, 5 kg)	
POE-DF610	MITSUI Japanese	MFI: 1.2 g/10 min	
HDPE-F600	Petrochemic corp, Korea	MFI: 0.05 g/10 min	5.0×10^5
HDPE-5000s	Daqing petrochemic corp, China	MFI: 1.1 g/10 min	3.3×10^5
HDPE-2200J	Daqing petrochemic corp, China	MFI: 5.5 g/10 min	2.3×10^5
HDPE-8916	Maoming petrochemic corp, China	MFI: 10 g/10 min	1.3×10^5
HDPE-2911	Fushun petrochemic corp, China	MFI: 20 g/10 min	1.2×10^5
SBS-1401	Yanhua petrochemic corp, China	S/B (weight ratio) = 40/60 MFI: 0.5 g/10 min	

Sample Preparation

All the blends were conducted in a two-screw extruder at 150–210°C, and then injection molded by using an injection machine PS40E5ASE (Japan) at 180–210°C to obtain standard specimens for mechanical properties tests. The blend compositions with their sample codes are listed in Table 2.

Tensile Strength

Standard tensile tests were conducted on dumbbell shaped specimens using an AG-10 TA tensile testing machine at room temperature. Test speed was kept at 20 mm/min, according to GB/T 1040-92 standard.

Table 2. Sample code and composition of the blends in present study

Sample code	Composition	MFI of HDPE (g/10 min)
PE-0.058	PS/POE/HDPE/SBS (80/20/5/5)	0.05
PE-1.1	PS/POE/HDPE/SBS (80/20/5/5)	1.1
PE-5.5	PS/POE/HDPE/SBS (80/20/5/5)	5.5
PE-10	PS/POE/HDPE/SBS (80/20/5/5)	10
PE-20 (5PE)	PS/POE/HDPE/SBS (80/20/5/5)	20
10PE	PS/POE/HDPE/SBS (70/20/10/5)	20
20PE	PS/POE/HDPE/SBS (60/20/20/5)	20
30PE	PS/POE/HDPE/SBS (50/20/30/5)	20

DSC Experimental

A Perkin Elmer DSC-7 was used to investigate the influence of HDPE molecular weight on the crystallization behavior of the as-prepared blends. The test samples (about 5 mg) were heated to 190°C at a heating rate of 10 K/min and then held at 190°C for 3 min to eliminate the thermal history. The cooling curves were recorded from 190°C to room temperature at a cooling rate of 10 K/min. All measurements were conducted under a nitrogen atmosphere. The crystallinity X_c of component i in the blends can be normalized by the equation,

$$X_c = \frac{\Delta H_i}{\Delta H_i^m \Phi_i}$$

where ΔH_i is the enthalpy of fusion of component i , directly obtained from DSC, and Φ_i is the mass fraction of component i in the blends. The enthalpy of fusion ΔH_i^m of 100% crystalline polymer is 293 J/g for HDPE^[35].

Scanning Electron Microscope (SEM)

A JEOL JSM-5900LV SEM instrument was used to examine the morphology of the fractured surfaces and the dispersed domains in the matrix using an acceleration voltage of 20 kV. The fractured surfaces of the specimens were sputter coated with a thin gold layer prior SEM examination. The samples were cryogenically fractured in the direction perpendicular or parallel to flow direction in liquid nitrogen.

For the systems with a drop/matrix structure, the average sizes of the dispersed droplets are determined. About 60–100 droplets were analyzed for each SEM photograph. The number average droplet diameter (D_n) was calculated from the equation:

$$D_n = \frac{\sum_i n_i d_i}{\sum_i n_i}$$

where n_i indicates the number of droplets having d_i as their diameter.

RESULTS AND DISCUSSION

DSC Results

The cooling and heating curves obtained for PS/POE/HDPE/SBS (80/20/5/5) quaternary blends with various HDPE of different MFI are shown in Fig. 1. The HDPE component exhibits mainly three small crystallization peaks in the cooling curves (Fig. 1a). A phenomenon of fractionated crystallization of the HDPE component follows in such a way that the HDPE crystallization occurs in at least three distinct steps. These three crystallization peaks might be originated by the presence of three different heterogeneities in HDPE droplets.

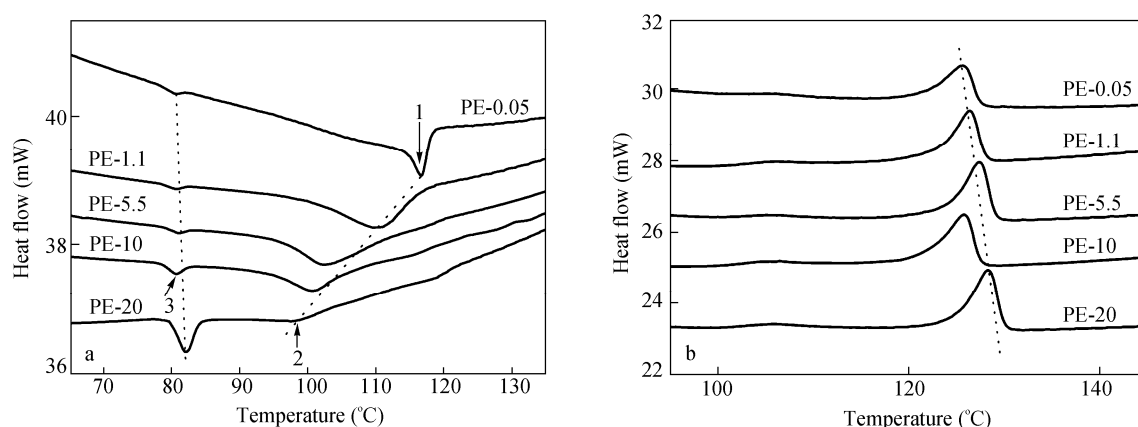


Fig. 1 DSC curves of PS/POE/HDPE/SBS (80/20/5/5) blends: (a) cooling and (b) heating. The MFIs of HDPE are 0.05 g/10 min, 1.1 g/10 min, 5.5 g/10 min, 10 g/10 min and 20 g/10 min, respectively.

The first peak at approximately the bulk crystallization temperature of HDPE is at about 120°C. The second peak is located at temperature around 100°C which may be formed because of the other type or less active nucleus in the HDPE particles. The last small peak is at about 80°C which could be attributed to crystallization *via* homogenous nucleation. According to Turnbull's approximate relation^[36] $T_{c,hom} = 0.8T_E$, where $T_{c,hom}$ is the crystallization temperature induced by homogeneous nucleation and T_E is the melt/crystallization equilibrium temperature. For polyethylene, the lowest crystallization temperature reported for homogeneous nucleation is around 70°C^[37]. The crystallization temperature peak at about 120°C becomes to shift to lower temperature on addition of HDPE with decreased molecular weight (increased MFI). For example, the peak of higher temperature at *ca.* 118°C in the blends with HDPE of high molecular weight [low MFI (0.05 g/10 min)] becomes to shift to the lower temperature at 100°C in the blends with HDPE of lower molecular weight [higher MFI (20 g/10 min)]. Meanwhile, the homogeneous crystallization peak at about 80°C becomes obvious with decreasing molecular weight (increased MFI) of HDPE. The crystallinity of HDPE with different MFI in PS/POE/HDPE/SBS 80/20/5/5 blends was calculated, which is in a range of 40%–50%, with change of MFI.

The melting curves of corresponding samples are shown in Fig. 1(b). It is interesting to find that samples with lower molecular weight (higher MFI) HDPE, which show obvious fractionated crystallization behavior and crystallization at a lower temperature, have a higher melting temperature. For samples crystallizing at a large degree of supercooling, only small and imperfect crystal structures could be developed. Thus the shift of the melting peak towards higher temperatures for samples with lower molecular weight (higher MFI) HDPE is most probably related to the reorganization of smaller and imperfect crystalline lamellae during the heating process.

SEM Microstructure

Figure 2 shows the SEM micrographs of PS/POE/HDPE/SBS (80/20/5/5) blends with HDPE of different MFI. The HDPE domains are indicated by the arrows in the figure. It is clearly shown that the domain size of dispersed HDPE phases with higher molecular weight [lower MFI (MFI: 0.05 g/10 min)] is much larger than that of HDPE with lower molecular weight [higher MFI (MFI: 20 g/10 min)] in PS/POE/HDPE/SBS (80/20/5/5) quaternary blends. For sample with higher MFI HDPE, the droplet diameter varies from 0.12 µm to 0.31 µm, and the average droplet diameter is 0.21 µm. For sample with lower MFI HDPE, the size of droplets varies from 0.38 µm to 1.64 µm, and the average droplet size is 0.72 µm.

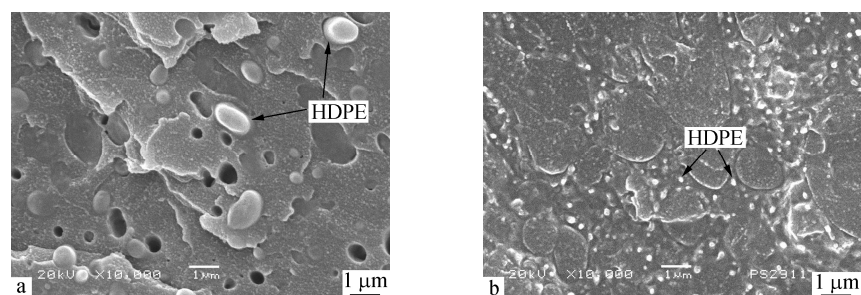


Fig. 2 SEM micrographs of PS/POE/HDPE/SBS (80/20/5/5) blends
a) MFI of HDPE: 0.05 g/10 min; b) MFI of HDPE: 20 g/10 min

The larger droplets contain more heterogeneities and can crystallize at low degree of supercooling, corresponding to the bulk crystallization temperature of HDPE. On the other hand, the smaller drops contain less active heterogeneities, can only crystallize at large degree of supercooling, corresponding to the fractionated crystallization behavior of HDPE. As a consequence of this, there are a significant number of droplets that do not contain active heterogeneities and will crystallize *via* homogenous nucleation at about 80°C. The lack of active heterogeneity in the smallest HDPE drops plays a major role in the occurrence of homogenous nucleation.

Effect of HDPE Content on Crystallization of PS/POE/HDPE/SBS Quaternary Blends

To investigate the effect of HDPE content on its domain size, and the fractionated crystallization behavior, the PS/POE/HDPE/SBS blends with the lowest molecular weight [highest MFI HDPE (MFI = 20 g/min)] are chosen, but the content of HDPE is changed. The cooling and heating curves of samples with changed HDPE content are shown in Fig. 3. It can be seen that HDPE content has a pronounced effect on the crystallization behavior of the blends. Though the fractionated crystallization can be observed for all blends, only blends with lower contents of HDPE show an obvious homogeneous nucleation at around 80°C. The ability of heterogeneous crystallization is strengthened by increasing of HDPE content. The extent of homogeneous crystallization could be stronger than the bulk crystallization when the HDPE content is ranging from 5 wt% to 10 wt% due to the smaller size of HDPE domains. One observes a big bulk crystallization peak at *ca.* 118°C as the HDPE content reaches to 20 wt%. With further increase of HDPE content to 30 wt%, only bulk crystallization peak at *ca.* 118°C is observed, and the crystallization caused by homogeneous nucleation at around 80°C can be ignored. The crystallinity of HDPE with different content in these blends was calculated, and not much change of crystallinity of HDPE was found (around 50%) with the increasing of HDPE content. On the other hand, all the blends show almost a constant melting point, disregarding the HDPE content used, as shown in Fig. 3(b).

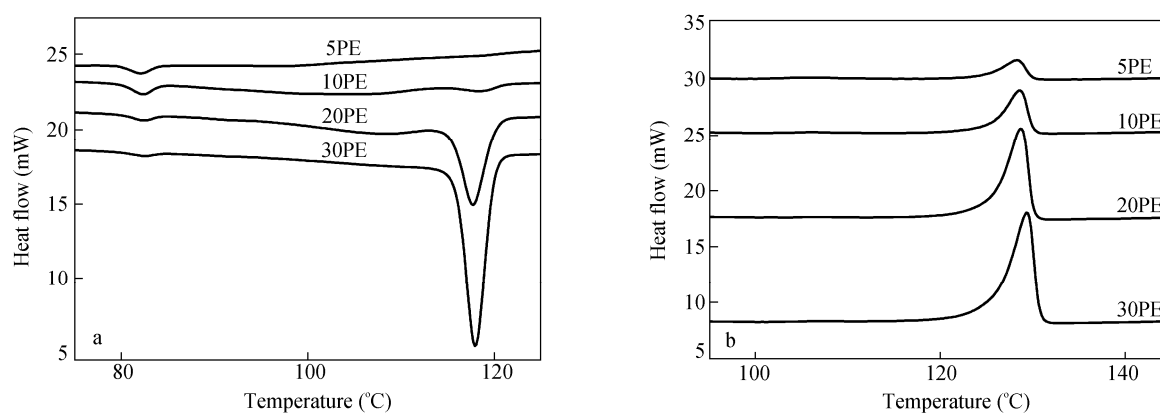


Fig. 3 DSC curves for PS/POE/HDPE/SBS blends: (a) cooling and (b) heating

Figure 4 shows the SEM micrographs of samples containing 10 wt%, 20 wt% and 30 wt% of HDPE, respectively. HDPE domains were indicated by the arrows in the figure. A clear droplet-in-matrix morphology (Fig. 2b) is observed at 5 wt% content of HDPE. Blends containing 10 wt% content of HDPE still exhibit a droplet-in-matrix morphology (Fig. 4a). With increasing of HDPE content to 20 wt%, one observes a coexistence of sea-island and co-continuous structures, which is a sign of the beginning of the phase inversion (Figs. 4b–4e). An enlarged complex sub-inclusions morphology can be seen in this blends, which has been reported by several authors^[38, 39]. In the blends with higher HDPE content of HDPE up to 30%, a very strong phase inversion region with totally co-continuous phase morphology is observed (see Fig. 4f).

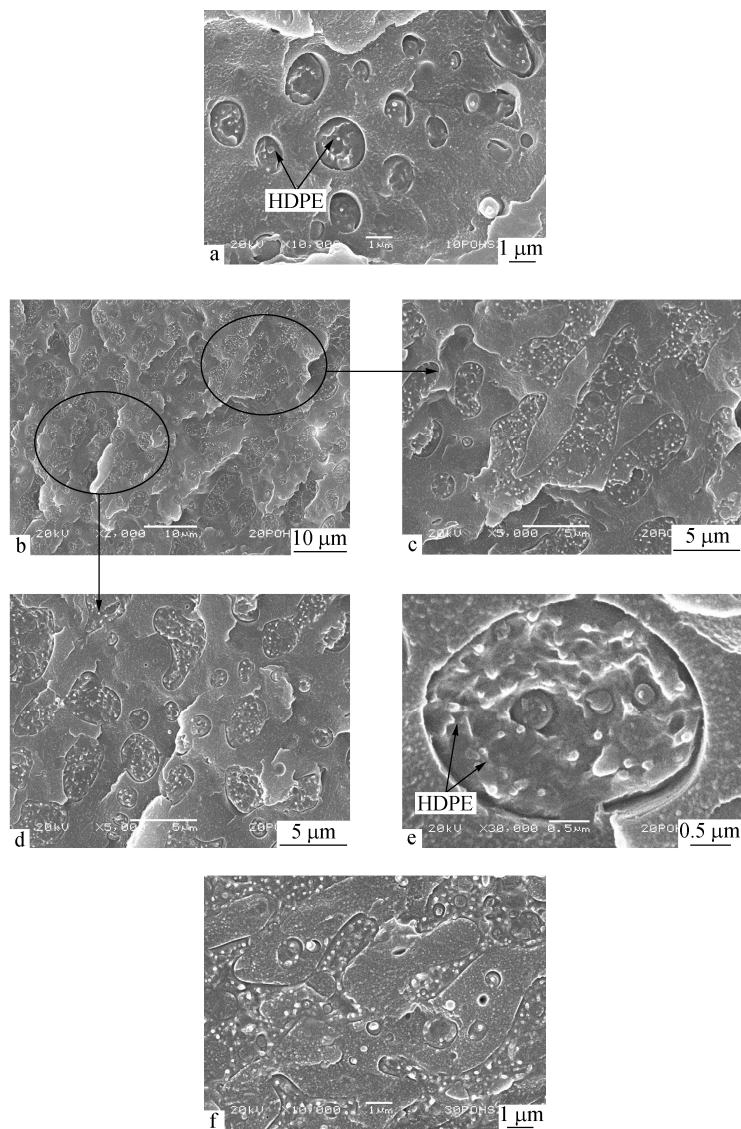


Fig. 4 SEM micrographs of 10PE, 20PE and 30PE blends

a) 10PE; b) Global overview of coexistence of co-continues and sea-island structures of 20PE blends; c) Enlarged co-continues phase of 20PE blends; d) Enlarged sea-island phase of 20PE blends; e) Enlarged complex composition-like phase morphology with inclusions of HDPE within POE phase of 20PE blends; f) 30PE blends

The stress-strain curves of PS/POE/HDPE/SBS quaternary blends with different HDPE contents are shown in Fig. 5. Apparently, both 5PE and 10PE blends exhibit a brittle fracture with low elongation. While the tensile toughness increases sharply with increasing of HDPE content up to 20%. This might be probably related to the crystallization behavior of HDPE and phase morphology of the blends changed with the HDPE content in the blends. One observes a phase inversion and less obvious fractionated crystallization when the HDPE content reaches to 20 wt%. With further increasing of HDPE content to 30%, a higher tensile toughness is observed, probably due to a totally co-continuous phase morphology and the dominated fractionated crystallization behavior.

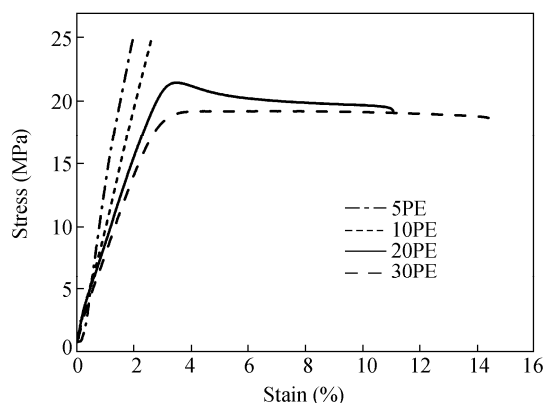


Fig. 5 Stress-strain curves of PS/POE/HDPE/SBS quaternary blends

CONCLUSIONS

In summary, the very interesting fractionated crystallization of minor dispersed HDPE phases in PS/POE/HDPE/SBS quaternary blends has been found, with appearance of three crystallization temperatures during cooling. As the MFI of HDPE is low (or molecular weight is high), the fractionated crystallization behavior is dominated by heterogeneous nucleation, and crystallization takes place mainly at a higher temperature around 120°C. Otherwise, the crystallization is dominated by homogeneous nucleation and occurs mainly at a lower temperature around 80°C. With increasing of HDPE content, a change of phase morphology from droplet to co-continuous structure is observed. As a result, the fractionated crystallization becomes less obvious, and only crystallization via heterogeneous nucleation at a higher temperature occurs. Correspondingly, a change of tensile toughness of the blends from brittle to ductile mode is observed.

REFERENCES

- 1 Barham, P.J., Jarvis, D.A. and Keller, A., *J. Polym. Sci.: Polym. Phys. Ed.*, 1982, 20(9): 1733
- 2 Cormia, R.L., Price, F.P. and Turnbull, D., *J. Chem. Phys.*, 1962, 37: 1333
- 3 Molinuevo, C.H., Mendez, G.A. and Müller, A.J., *J. Appl. Polym. Sci.*, 1998, 70: 1725
- 4 Everaert, V., Groeninckx, G., Koch, M.H.J. and Reynaers, H., *Polymer*, 2003, 44: 3491
- 5 Everaert, V., Groeninckx, G., Pionteck, J., Favis, B.D., Aerts, L., Moldenaers, P. and Mewis, J., *Polymer*, 2000, 41: 1011
- 6 Bose, S., Bhattacharyya, A.R., Kodgire, P.V. and Misra, A., *Polymer*, 2007, 48: 356
- 7 Cormia, R.L., Price, F.P. and Turnbull, D., *J. Chem. Phys.*, 1962, 37: 1333
- 8 Frensch, H., Harnischfeger, P. and Jungnickel, B.J., "Multiphase Polymers: Blends and Ionomers" (ACS Symp Series 395), American Chemical Society, Washington, 1989, p.101
- 9 Uriguen, J.I., Bremer, L., Mathota, V. and Groeninckx, G., *Polymer*, 2004, 45: 5961
- 10 Shi, D., Yin, J.H., Ke, Z., Gao, Y. and Li, R. KY., *J. Appl. Polym. Sci.*, 2004, 91: 3742

- 11 Tol, R.T., Mathot, V.B.F. and Groeninckx, G., *Polymer*, 2005, 46: 383
- 12 Yordanov, C. and Minkova, L., *Eur. Polym. J.*, 2005, 41: 527
- 13 Pompe, G., Pötschke, P. and Pionteck, J., *J. Appl. Polym. Sci.*, 2002, 86: 3445
- 14 Arnal, M.L., Müller, A.J., Maiti, P. and Hikosaka, M., *Macromol. Chem. Phys.*, 2000, 201: 2493
- 15 Müller, A.J., Balsamo, V., Arnal, M.L., Jakob, T., Schmalz, H. and Abetz, V., *Macromolecules*, 2002, 35(8): 3048
- 16 Balsamo, V. and Gouveia, L., *J. Polym. Sci.: Part B: Polym. Phys.*, 2007, 45: 1365
- 17 Morales, R.A., Arnal, M.L. and Müller, A.J., *Polym. Bull.*, 1995, 35: 379
- 18 Klemmer, N. and Jungnickel, B.J., *Colloid Polym. Sci.*, 1984, 262: 381
- 19 Morales, R.A., Arnal, M.L. and Müller, A.J., *Polym. Bull.*, 1995, 35: 379
- 20 Yordanov, C. and Minkova, L., *Eur. Polym. J.*, 2005, 41: 527
- 21 Kong, J., Fan, X.D. and Jia, M., *J. Appl. Polym. Sci.*, 2004, 93: 2542
- 22 Long, Y., Stachursky, Z.H. and Shanks, R.A., *Polym. Int.*, 1991, 26: 143
- 23 Bernal-Lara, T.E., Liu, R.Y.F., Hiltner, A. and Baer, E., *Polymer*, 2005, 46: 3043
- 24 Băiltoul, M., Saint-Guirons, H., Xans, P. and Monge, P., *Eur. Polym. J.*, 1981, 17: 1281
- 25 Morales, R.A., Arnal, M.L. and Müller, A.J., *Polym. Bull.*, 1995, 35: 379
- 26 Arnal, M.L., Matos, M.E., Morales, R.A., Santana, O.O. and Müller, A.J., *Macromol. Chem. Phys.*, 1998, 199: 2275
- 27 Buekens, A.G. and Resources, H.H., *Conservation and Recycling*, 1998, 23: 163
- 28 Ross, S. and Evans, D., *Cleaner Production*, 2003, 11: 561
- 29 Kaminsky, W., Predel, M. and Sadiki, A., *Polym. Degrad. Stab.*, 2004, 85: 1045
- 30 Tang, L.W., Tam, K.C., Yue, C.Y., Hu, X., Lam, Y.C. and Li, L., *Polym. Int.*, 2001, 50: 95
- 31 Jelcic, Z., Holjevac-Grguric, T. and Rek, V., *Polym. Degrad. Stab.*, 2005, 90: 295
- 32 Tang, L.W., Tam, K.C., Yue, C.Y., Hu, X., Lam, Y.C. and Li, L., *J. Appl. Polym. Sci.*, 2004, 94: 2071
- 33 Gao, G.H., Zhou, C., Yang, H.D. and Zhang, H.X., *J. Appl. Polym. Sci.*, 2007, 103: 738
- 34 Fu, X.T., Ding, M.M., Tang, C.Y., Li, B., Zhao, Z.Y., Zhang, Q., Long, H., Tan, T.W. and Fu, Q., *J. Appl. Polym. Sci.*, in press
- 35 Wunderlich, B., "Thermal Analysis", Academic Press, New York, 1990, p.418
- 36 Turnbull, D. and Cech, R.E., *J. Appl. Phys.*, 1950, 21: 804
- 37 Arnal, M.L. and Müller, A.J., *Macromol. Chem. Phys.*, 1999, 200: 2559
- 38 Everaert, V., Groeninckx, G. and Aerts, L., *Polymer*, 2000, 41: 1409
- 39 Everaert, V., Aerts, L. and Groeninckx, G., *Polymer*, 1999, 40: 6627